

ICOM COMMITTEE FOR CONSERVATION

9th Triennial Meeting
Dresden, German
Democratic Republic
26–31 August 1990

Preprints Volume I



COMITÉ DE L'ICOM POUR LA CONSERVATION



I have not yet seen the
 original of the letter from
 Mr. [Name] to Mr. [Name]
 which you mention in your
 letter of the 10th inst.
 but I have seen the copy
 which you have made of it
 and it is a very good one
 and I am glad to hear
 that you have it.

A NOTE ON THE COVER

This view of Dresden from the right bank of the Elbe, below the Augustus Bridge, is by Canaletto. The etching, from 1748, is reproduced courtesy of the Dresden Kupferstichkabinett. Photography by Deutsche Fotothek, an office of the Sächsische Landesbibliothek, Dresden.

NOTES SUR LA COUVERTURE

Ce panorama de Dresde, vu de la rive droite de l'Elbe sous le pont Augustus, est dû à Canaletto. La gravure, datant de 1748, est reproduite avec la gracieuse permission du Dresden Kupferstichkabinett. Photo par Deutsche Fototek, département de la Sächsische Landesbibliothek, Dresde.

ICOM COMMITTEE FOR CONSERVATION
Preprints 1990



ICOM COMMITTEE FOR CONSERVATION

9th Triennial Meeting
Dresden, German
Democratic Republic
26-31 August 1990

Preprints

ICOM Committee for Conservation
Los Angeles
1990

CONS.
N
8554.5
IG1
C73
1990
v.1
c.1

ACKNOWLEDGEMENTS

This publication has been made possible through the generous support of the Samuel H. Kress Foundation and by a grant from the Union Carbide Corporation. The ICOM Committee for Conservation recognizes with gratitude these contributions to the proceedings.

The Preprints Editor also wishes to thank all of those who have contributed their ideas and services toward making this edition a success. This long list begins with the Working Group Coordinators, who provide the crucial link in the editorial process by soliciting and editing the papers from their authors. It is no exaggeration to say that without their cooperation there would be no publication, and they deserve every recognition for this service.

The members of the Review Committee—David Grattan, Gerry Hedley, Nicholas Stanley Price, and Sue Walston—deserve special thanks for undertaking the job of finalizing the contents of this edition. Grateful acknowledgment also goes to the Getty Conservation Institute for under-

writing the costs of the Review Committee meeting.

As with the Sydney edition, the Preprints authors have once again eased the Editor's job by attending so carefully to their grid sheets and cooperating with the deadlines. Special thanks also go to several individuals. For this edition Renée Mandel provided essential administrative support at every stage in the process. JoAnn Hill and Corinne Lightweaver furnished proofreading and other editorial assistance whenever help was needed.

Finally, a word of appreciation goes to Janet Bridgland, Chairman of the Committee, and to the members of the Directory Board for initiating and supporting the changes realized in this edition.

—K.G.

EDITOR
Kirsten Grimstad

DESIGN
Sheila Levrant de Bretteville

PRODUCTION
Jennifer Egger
Vivian Chow

TYPESETTING
Mondo Typo

PRINTING
Franklin Press

Copyright © 1990
International Council of Museums
Copyright of individual papers
remains with the authors.
Published by the ICOM
Committee for Conservation, 1990
ISBN 0-89236-185-9
Printed in the United States
of America

Available from:

International Council of Museums
1 rue Miollis
75732 Paris Cedex 15
France

ICCROM
13 via di San Michele
00153 Rome
Italy

The Getty Conservation Institute
4503 Glencoe Avenue
Marina del Rey, CA 90292-6537
U.S.A

THE GETTY CENTER
LIBRARY

Contents/Table des Matières

Volume 1 Working Group 1

Introduction

Scientific Examination of Works of Art/Investigation

scientifique des oeuvres d'art

- 3 Ingrid C. Alexander and Jacqueline S. Olin, *Examining Albert Pinkham Ryder's Preparatory Sketch and Compositional Changes by Neutron Induced Autoradiography*
- 9 Michele R. Derrick and Dusan C. Stulik, *Identification of Natural Gums in Works of Art Using Pyrolysis-Gas Chromatography*
- 14 Klara Erdőhalmi-Török and Marta Kissné Bendefy, *Microscopic Investigations of 19th Century Darkened Painting Samples*
- 18 Myriam Eveno, Dominique Fromageot, Bruce Kusko et Christian Lahanier, *Etude de l'altération d'une plaque émaillée attribuée à la production de Limoges*
- 24 V. P. Golikov and V. N. Kireyeva, *Study of Spatial Distribution of Protein Bindings in Situ by Means of Reactive Dyes*
- 29 V. P. Golikov and Z. F. Zharikova, *Analysis of Spatial Distribution of Hydrophobic Restoration Materials by Means of Fluorescent Probes*
- 33 Galina N. Gorokhova and Marianna G. Kononovitch, *The Materials for Painting Used by the Russian and Foreign Painters Who Worked in Russia in the 18th Century*
- 35 Masamitsu Inaba, Jun-ichi Miyata, and Ryuitiro Sugisita, *Micro X-Ray Diffractometer (PSPC/MDG) System for the Study of Works of Art*
- 38 Peter Klein, *Tree-Ring Chronologies of Conifer Wood and Its Application to the Dating of Panels*
- 41 Peter Klein and Friedrich-Wilhelm Bröker, *Investigations on Swelling and Shrinkage of Panels with Wooden Support*
- 44 Alexander J. Kossolapov, *The X-Ray Fluorescent Imaging of Works of Art*
- 47 E. A. Luybavskaya, *Investigation of Properties of Protein Glues*
- 51 Christian Neelmeijer, Hans-Peter Schramm, Helmut Matthes, and Christine Wendt, *Nondestructive Multielement Analysis of Art Objects—Opportunities for the Application of the External PIXE/PIGE Technique*
- 57 Marianne Odlyha, *A Novel Approach to the Problem of Characterizing the Binding Media in Early Italian Paintings (13th/16th Century)*
- 62 Enrique Parra and Andrés Serrano, *Chemical Analysis of Wax Seals and Dyed Textile Attachments from Parchment Documents: Preliminary Investigations*
- 68 S. A. Pisareva and Yu. I. Grenberg, *Russian 17th–18th Century Production Formulas for Blue and Green Copper Pigments*
- 72 Raffaella Rossi-Manaresi and Antonella Tucci, *Painting Technique of Cima da Conegliano and Analytical-Documentary Comments about Pigments*
- 79 Naoko Sonoda, Elisabeth Martin et Alain R. Duval, *Utilisation des microscopes optique et électronique pour l'étude des préparations blanches de tableaux italiens sur bois*
- 83 Luiz A. C. Souza et Marília O. S. Pereira, *Etude technique des six peintures attribuées à maître Athayde, le peintre le plus important de la période baroque/rococo à Minas Gerais, Brésil*
- 88 M. Tseitlina and N. Kozhukh, *Luminescence Study of Protein Binders Used in Painting*

- 90 Anne van Grevenstein, Karin Groen, J.R.J. van Asperen de Boer, Liesbeth Abraham, and Koos Levy-van Halm, *Aspects of the Restoration and Technical Examination of the Haarlem Civic Guard Group Portraits by Frans Hals*
- 95 V. N. Yarosh, *Analysis of Painting Binding Materials Containing Polysaccharides by Photometry Methods as well as by Paper and Liquid Column Chromatography*
- 99 Petr Zalabák, Zdeněk Urbanec, and Jiří Čejka, *The Application of IBM Personal Computers (IBM PC) for Mathematical Evaluation of X-Ray Diffraction Data in Preservation and Scientific Reassessment of Museum Collections*

Working Group 2

Structural Restoration of Paintings on Canvas/Restoration structurale des peintures sur toile

- 107 Gustav A. Berger and William H. Russell, *Changes in Resistance of Canvas to Deformation and Cracking (Modulus of Elasticity "E") as Caused by Sizing and Lining*
- 113 Franco Del Zotto, *Preservation of Canvas Paintings: Structural Solutions in Relation to Environmental Changes*
- 119 Gerry Hedley, Caroline Villers, Robert Bruce-Gardner, and Rhona Macbeth, *A New Method for Treating Water Damage Flaking*
- 124 Frantisek Makes, *Enzymatic Hydrolysis of the Lining Paste in Eeckhout Picture "Joseph and His Brothers" by Krill Enzymes*
- 130 I. V. Nazarova, E. L. Malachevskaya, and L. I. Yashkina, *Technique of Restoring Paintings on Canvas without Lining*
- 133 Ingo Sandner, *The Treatment of Cracks in Canvas Paintings with Synthetic Adhesives—Procedures and Possible Combinations with the Lining Process*
- 139 Volker Schaible, *Réflexions sur la formation de cuvettes à la surface des peintures sur toile*
- 145 Puccio Speroni, *A Transportable Suction Table for On-the-Spot Conservation of Large Sized Paintings*

Working Group 3

Ethnographic Materials/Matériaux ethnographiques

- 151 Penelope C. Edmonds, *Fungi and Its Relationship with Aboriginal Painted Surfaces Containing the PVAc Emulsion Binder "Aquadhere"*
- 157 Sue Gatenby, *An Investigation into Cleaning Procedures for Mould Stained Australian Aboriginal Objects Painted with Modern Media*
- 163 Eric F. Hansen, Eileen T. Sadoff, and Rosa Lowinger, *A Review of Problems Encountered in the Consolidation of Paint on Ethnographic Wood Objects and Potential Remedies*
- 169 S.A.M. Monowar Jahan, *Material Culture Studies of Dacca Muslin*
- 174 Colette Jourdain, *Méthodes traditionnelles et locales de conservation des objets ethnographiques dans diverses régions africaines*

Working Group 4

Documentation/Documentation

- 181 Jessica S. Brown, *Report from AATA: Collaborative Activities*
- 185 Suzanne Keene, *Management Information for Conservation*
- 192 Kathleen McDonnell, *Conservation Information Network: The Getty Conservation Institute's Evolving Role*
- 196 James D. Roberts, *A Multi-Task Database for Condition Survey, Conservation Reports, and Laboratory Management*
- 199 Barbara L. Snyder, *Conceptualizing a Conservation Thesaurus*
- 203 E. S. Soldatenkov, *Computer in a Restoration Workshop*

Working Group 5

Polychromed Sculpture/Sculpture polychrome

No program this triennial period.

Working Group 6

Modern and Contemporary Art/Art moderne et contemporain

- 211 Pinin Brambilla Barcilon and Antonietta Gallone Galassi, *White Paintings by Lucio Fontana: Investigation and Scientific Examinations*
- 214 Matthijs de Keijzer, *A Brief Survey of the Synthetic Inorganic Artists' Pigments Discovered in the Twentieth Century*
- 220 Matthijs de Keijzer, *Microchemical Analysis on Synthetic Organic Artists' Pigments Discovered in the 20th Century*

Working Group 7

Wet Organic Archaeological Materials/Matériaux organiques archéologiques gorgés d'eau

- 229 Per Hoffmann, *A Waterlogged Medieval River Craft from the Rhine Stabilized in a Two-Step Polyethylene Glycol Treatment*
- 234 Setsuo Imazu and Tadateru Nishiura, *A New Freeze-Drying Method Using Mannitol and PEG for the Preservation of Waterlogged Wood*
- 239 A. L. Kirillov and E. A. Mikolajchuk, *Quantitative Estimation of Archaeological Wood Degradation Degree by Infra-Red Fourier Transform Spectroscopy*
- 241 András Morgós and Lucia Glattfelder-McQuirk, *The Sucrose Conservation of 15th-16th Century Waterlogged Wooden Finds*
- 243 Tim Padfield, Janne Winsløw, Walter Batsberg Pedersen, and Jens Glastrup, *Decomposition of Polyethylene Glycol (PEG) on Heating*

Working Group 8

Photographic Records/Documents photographiques

- 249 Klaus B. Hendriks and Sebastian Dobrusskin, *The Conservation of Painted Photographs*
- 255 Bertrand Lavédrine et Françoise Flieger, *Les aristotypes, Ière partie: technologie, conservation et analyse au M.E.T. des premiers papiers photographiques industriels à émulsion*
- 262 Mark H. McCormick-Goodhart, *The Multilayer Structure of Tintypes*
- 268 Douglas W. Nishimura, *Improvements to the Photographic Activity Test in ANSI IT9.2*

Working Group 9

Textiles/Textiles

- 277 Mary W. Ballard, Robert J. Koestler, and Norman Indictor, *Recent Results Concerning the Degradation of Historic Silk Flags*
- 283 Eva Fischer and Brigitte Krüger, *Conservation and Restoration of a Double-Leaf Standard—Silk Ground with Relief Embroidery*
- 289 V. P. Golikov, *Technology of Dyeing Silk by Cochineal: Part 1. Theoretical Analysis of the Problem and Development of Investigation Methods*
- 294 V. P. Golikov and I. I. Vishnevskaya, *A Comparative Study of Dyeing Technology in 16th-17th Century Persian and Turkish Textiles from Moscow Kremlin Collection*
- 299 Márta Járó, Attila Tóth, and Erzsébet Gondár, *Determination of the Manufacturing Technique of a 10th Century Metal Thread*
- 302 Kyung Sook Jeon and Ira Block, *Photodegradation of Cellulosics, Part 1: Effects of Temperature and Humidity on Tear Strength Retention*
- 307 Michaela Keyserlingk, *The Use of Adhesives in Textile Conservation*

- 313 Yvonne Shashoua, *Investigation into the Effects of Cleaning Natural Woven Textiles by Aqueous Immersion*

Working Group 10

Stone/Matériaux pierreux

- 321 A. Elena Charola, Johannes Weber, and Erica Bolle, *Preliminary Studies of Deterioration Patterns at Cerro Colorado, Argentina: Open Cave Formation and Honeycomb Weathering*
- 326 Fatma M. Helmi, *Study of Salt Problem in the Sphinx, Giza, Egypt*
- 330 Wolfram Köhler, *Structure Changes of Weathered Carrara Marble Sculptures as a Function of Their Destructioned Position*
- 336 Lorenzo Lazzarini and Gianni Lombardi, *Bentonite for Cleaning and Desalination of Stones*
- 340 Janusz Lehmann, *Conservation of Medieval Stone Relics under the Cathedrals of Gniezno, Poland*
- 343 Yuri A. Lyubchenko, *The Problem of Conservation Treatment of the Unique Gypsum Sculpture with Due Regard for Its Possible Repeated Displacement*
- 347 Yu. P. Petushkova and A. F. Grishkova, *Bacterial Degradation of Limestone Treated with Polymers*
- 350 Josef Pühringer and Johannes Weber, *A Hypothetical Contribution to the NO_x Problem in Calcareous Stone*
- 355 Josef Pühringer and Johannes Weber, *A Model for Salt Extraction: Some Principles*
- 361 Josef Pühringer and Johannes Weber, *Salt Action and Material Testing*
- 366 Todor Stambolov, *The Synergism of Ammonia and Sulphur Dioxide in the Erosion of Monuments by Acid Rain*

Working Group 11

Theory and History of Restoration/Théorie et histoire de la restauration

- 373 Yu. G. Bobrov, *The Laws of Perception and Regularities of Restoration of Artistic Monuments*
- 378 Barbara Whitney Keyser, *History of Conservation and the Teaching of Museology*
- 383 L. I. Popova, *Problems of Ethics in Russian (19th Century) and Soviet Restoration Based on National Painting Materials*
- 388 Carlos Rua and Anton Rajer, *The Bolivian National Art Conservation Center: Its History and Organization*
- 391 B. Ya. Stavisky, *Protection and Restoration of Cultural and Artistic Monuments of Central Asia in the Pre-War Decade (1929-1941)*
- 396 O. V. Yakhont, *Methods Aspects of Restoration Completions*

Working Group 12

Care of Works of Art in Transit/Protection des oeuvres d'art pendant le transport

- 401 Peter Cannon-Brookes, *The Transportation by Sea from Southampton to Cape Town of Oil Paintings in a Container with Environmental Monitoring*
- 405 Nobuyuki Kamba, *Variations in Relative Humidity and Temperature as Measured in a Packing Case*
- 410 Mervin J. Richard, *Packing Delicate Art Objects for Transit*
- 415 David Saunders and Richard Clarke, *Monitoring the Environment within Packing Cases Containing Works of Art in Transit*
- 423 Shelley G. Sturman and Judy L. Ozone, *The Courier Experience*

Working Group 13

Natural History Collections/Collections d'histoire naturelle

- 431 C. V. Horie, *Fading of Feathers by Light*
- 437 Society for the Preservation of Natural History Collections—Conservation Committee, Assessment Subcommittee, *Defining Standard Procedures for Assessing the Condition of a Fluid-Preserved Collection*

Working Group 14

Graphic Documents/Documents graphiques

- 443 Gerhard Banik, *Conservation of Water Damaged Museum and Archival Documents*
- 447 Helen D. Burgess, *The Stabilization of Cellulosic Fibres by Borohydride Derivatives*
- 453 Paolo Salvini and Gianni Martinelli, *Numerical Processing of Fourier Transform Infrared Spectra: A Powerful Tool in Paper Analysis*
- 456 S. A. Dobrusina, *Increasing the Durability of Paper When Restoring Documents by Paper Pulp Filling Process*
- 459 M. C. Enshaian, *A propos du montage après restauration d'un dessin de grand format: le poncif et l'étude du personnage de Napoléon pour le Tableau du Sacre par J. L. David*
- 463 Verena Flamm, Christa Hofmann, Sebastian Dobruskin, and Gerhard Banik, *Conservation of Tracing Papers*
- 468 Susy Hebblethwaite, Mauro Matteini, Letizia Montalbano, Maria Grazia Vaccari et Nathalie Ravanel, *Recensement des papiers peints en Italie—Problèmes de conservation et de montage*
- 472 Christa Hofmann, Verena Flamm, Gerhard Banik, and Kurt Messner, *Bleaching of Foxing Stains in Art Nouveau Prints*
- 478 J. P. Nyuksha, O. A. Gromov, and J. V. Pokrovskaja, *Mass Processing of Documents for Fungi Contamination Control*
- 482 Pascale Richardin, Françoise Fliedner, Sylvette Bonnassies, and Claude Pepe, *Analyse par CG/SM des produits d'imprégnation de papiers calques anciens*
- 489 Maria Carme Sistach, *Scanning Electron Microscopy and Energy Dispersive X-Ray Microanalysis Applied to Metallogallic Inks*
- 495 Jan Wouters, Gely Gancedo, An Peckstadt, and Lieve Watteuw, *The Codex Eyckensis: An Illuminated Manuscript on Parchment from the 8th Century A.D. Laboratory Investigation and Removal of a 30-Year-Old PVC Lamination*
- 500 Mariagrazia Plossi Zappalà, *Le propionate de calcium: agent désacidifiant et stabilisant des papiers anciens?*

Working Group 15

Mural Paintings and Mosaics/Peintures murales et mosaïques

- 507 Ivo Hammer and Ernst Lux, *Theory and Practice: Remarks on the Examination and Conservation of the Romanesque Mural Paintings in Salzburg Nonnberg*
- 513 Serguéi Kasparov and Svetlana Tamaéva, *Les nouvelles méthodes de refixage par injection dans les supports d'enduit des peintures murales*
- 518 Paolo Mora, Laura Mora et Eduardo Porta, *Conservation et restauration de la tombe de Néfertari dans la Vallée des Reines*
- 524 Colette Naud et Monica Martelli Castaldi, *Utilisation des absorbants pour le nettoyage des fresques*
- 530 M. M. Naumova and S. A. Pisareva, *New Data on Green Copper Pigments in Wall Paintings*
- 534 Eduardo Porta, Antoni Palet et Eudald Guillaumet, *Le bleu aérinte: un pigment méconnu en peinture murale romane*

- 539 Raffaella Rossi-Manaresi and Antonella Tucci, *The "Stories of Romulus and Remus": A Fresco Frieze by Carracci*
- 545 V. N. Yarosh and N. Yu. Zakharova, *Identification and Quantitative Analysis of Organic Materials in Ground Coats of Wall Paintings in Sultan Sanjar's Tomb*

Working Group 16

Resins: Characterization and Evaluation/ Résines: caractérisation et évaluation

- 551 David W. Grattan, *Parylene at the Canadian Conservation Institute: An Initial Survey of Some Applications*
- 557 Eric F. Hansen and Neville Agnew, *Consolidation with Moisture-Curable Isocyanates: Polyureas and Polyurethanes*
- 563 Christopher W. McGlinchey, *The Industrial Use and Development of Low Molecular Weight Resins: An Examination of New Products of Interest to the Conservation Field*
- 568 Richard E. Stone, Raymond White, and N. Indictor, *Surface Composition of Some Italian Renaissance Bronzes*

Working Group 17

Lighting and Climate Control/Eclairage et contrôle du climat

- 577 Eva E. Astrup and Kristin E. Hovin Stub, *Saturated Salt Solutions for Humidity Control of Showcases—Conditions for a Successful System*
- 583 Stefan Michalski, *Towards Specific Lighting Guidelines*
- 589 Stefan Michalski, *An Overall Framework for Preventive Conservation and Remedial Conservation*
- 592 Sadatoshi Miura, *Temperature and Humidity in a Large Glass Showcase for a Temple Hall (Part 2)*
- 596 Tim Padfield and Poul Jensen, *Low Energy Climate Control in Museum Stores*
- 602 Sarah Staniforth, *The Logging of Light Levels in National Trust Houses*

Working Group 18

Conservation of Leathercraft and Related Objects/ Conservation des cuirs artisanaux et objets similaires

- 611 Maria Cristina Berardi, Mara Nimmo, and Mariabianca Paris, *The Seventeenth-Century Flock-Leather Wall Hangings of the Chigi Chapel in Ariccia: A Case Study*
- 616 Marion Kite, *A 1740s Horse Hair Hat, a Busby c1827, and a Fur-Lined Cape c1936*
- 622 H.A.B. van Soest, *Sulphurous Substances in the Tanning of Leather with Vegetable Tannins*
- 626 Gregory S. Young, *Microscopical Hydrothermal Stability Measurements of Skin and Semi-Tanned Leather*

Working Group 19

Easel Paintings on Rigid Support/Peintures de chevalet sur supports rigides

- 635 Carmen Chizzola, *Restauration de miniatures: le collage des supports en ivoire à l'aide d'une construction appropriée en plexiglas*
- 641 Judit Edős, *Restoration of Two Icons Painted on Iron Plates in the Eastern Orthodox Church in Grábóc*
- 648 David C. Goist, *Case Study of an Early Dutch Landscape*
- 653 Vladimir G. Simonov, *The Method Used for Conservation Treatment of the Vietnamese Lacquer Sculpture "Donator"*
- 659 Hélène Verougstraete-Marcq et Roger Van Schoute, *Aspects technologiques de l'histoire de la peinture flamande: cadres et supports aux 15e et 16e siècles*

- 663 Jørgen Wadum, *17th Century Flemish Panel Makers' Red Chalk Master Marks*

Working Group 20

Glass, Ceramics, and Related Materials/Verres, céramiques et matériaux apparentés

- 669 S. M. Bradley, *Evaluation of Hxtal NYL-1 and Loctite 350 Adhesives for Glass Conservation*
- 675 Alice Boccia Paterakis, *A Preliminary Study of Salt Efflorescence in the Collection of the Ancient Agora, Athens, Greece*

Working Group 21

Training in Conservation and Restoration/Formation en conservation et restauration

- 683 Kulpanthada Janposri, *The Need for Training Personnel for the Conservation of Cultural Heritage in ASEAN Countries*
- 686 Gabriela Krist and Gerhard Banik, *Bibliography: Theses, Dissertations, Research Reports in Conservation*
- 689 Roland Möller, *The Training of Restorers for Historic Murals and Coloured Architectural Design at the Dresden Academy of Fine Arts*
- 692 Roger Price and Anne Moncrieff, *Conservation of Industrial Collections—A New Training Course*
- 696 Ingo Sandner, *Artistic Restorer or Restoration Engineer?*
- 700 Poppy Singer and Dinah Eastop, *Developing Student Assessment Techniques in Conservation Training*
- 704 N. Vlado, *Problems of Educating Restorers in the U.S.S.R.*

Working Group 22

Metals/Métaux

- 711 E. Bakaliarova, N. Timofeeva, M. Kalich et I. Kassatonova, *Alliages de cuivre en fonderie d'art: étude en matière de corrosion*
- 715 Jan-Erik Bergh, Maria Brunskog, and Mats Foghelin, *Corrosion on and Preservation of Ethnological Iron—Report from a Swedish Project*
- 721 Peter Burde, *Investigation and Restoration of the Gun Barrel of the "Golden Gun" of the 17th Century*
- 726 Hanna Jedrzejewska, *Analyses of Ancient Alloys: Retrospective Considerations*
- 732 Ian Donald MacLeod and Stephane Pennec, *The Effects of Composition and Microstructure on the Corrosivity of Copper Alloys in Chloride Media*
- 740 Alexander Ivanovich Minzhulin, *Restoration of Ancient Archaeological Granulation Jewelry*
- 745 William Mourey, *La protection des grosses pièces métalliques par création d'un couple galvanique, avenir ou utopie?*
- 748 Josef Pühringer and Bertil Johnsson, *An Alternative Preservation Method for Corroded Outdoor Bronzes*
- 754 N. Timofeeva, I. Kassatonova, F. Arakelian, E. Bakaliarova et B. Sizov, *Etudes complexes du monument à Minine et Pojarski*

Working Group 23

Icons/Icônes

- 763 Ivan Gorine, *La restauration des peintures d'icônes en URSS*
- 768 Olga Lélékova, *Problèmes de restauration des icônes russes*
- 773 D. Malcéva, *Certains aspects de la méthodologie dans le musée russe*

- 777 Zuzana Skálová, *Conservation Problems in Egypt: Icons, Preliminary Classification, and Some Case Studies*
- 783 A. I. Yakovleva, *Approaches to the Study of Methods Used in Medieval Face Painting*

Working Group 24

Rock Art/art rupestre

- 787 Jacques Brunet, Sylvie Demailly et Maria Conceicao Soares Meneses Lage, *Premiers résultats de l'étude des peintures rupestres de la Toca Do Boqueirao do sitio da Pedra Furada (Piaui, Brésil)*
- 793 Jean Vouvé, Maria Eugénia Van de Maele et Pierre Vidal, *Etude climatologique et hydrogéologique d'un tunnel de laves orné sous climat subtropical: cas de la caverne peinte d'Ana Kay Tangata (Ile de Pâques, Chili)*

Working Group 25

Control of Biodeterioration/Contrôle de la biodétérioration

- 801 Hideo Arai, Noritaka Matsumura, and Hiroyuki Murakita, *Induced Foxing by Components Found in Foxed Areas*
- 804 Mary T. Baker, Helen D. Burgess, Nancy E. Binnie, Michele R. Derrick, and James R. Druzik, *Laboratory Investigation of the Fumigant Vikane®*
- 812 Mark Gilberg, *Inert Atmosphere Disinfestation Using Ageless® Oxygen Scavenger*
- 817 Lim Chong Quek, Muhammadin Razak, and Mary W. Ballard, *Pest Control for Temperate vs. Tropical Museums: North America vs. Southeast Asia*
- 821 Nieves Valentin, *Insect Eradication in Museums and Archives by Oxygen Replacement: A Pilot Project*
- 824 Galina A. Zaitseva, Konstantin P. Zabotin, Andrej I. Kapranov, Igor Ja. Pavlinov, Polina D. Fraishtat, M. M. Shemjakin, *New Antifeedants for Pest Insects in Collections and Various Aspects of Their Use in Museums*

Working Group 26

Furniture/Meubles

- 831 Brian B. Considine, Michel Jamet, and Anna Østrup, *The Conservation of Two Pieces of Boulle Marquetry Furniture in the Collection of the J. Paul Getty Museum*
- 835 Gregory John Landrey, *The Use of Fluorescent Microscopy in Furniture Conservation*

Introduction

This Triennial Meeting of the ICOM Committee for Conservation marks a shift toward new organizational structure and procedures occasioned by the needs of a growing membership and participation in the organization. These changes concern the format of the Triennial Meeting, which now includes plenary sessions, and the selection of contents for this publication through a peer review process. While the Directory Board launched these initiatives, implementation has occurred only with the cooperation of the membership at all levels of the Committee.

In attempting to serve the organization better through this period of growth, it has been important to retain the spirit in which the Committee for Conservation's Triennial Meetings first came into being. The Committee was founded in Brussels in 1967 to consolidate the work of two related ICOM organizations which had been holding joint meetings for more than a decade: the Commission on the Care of Paintings and an International Subject Committee of Museum Laboratories. The earliest forerunner, the Commission on the Care of Paintings, was an association of museum directors and curators established in 1948 to gather and disseminate information on all aspects of the examination, recording, cleaning, and repair of painting and thus to encourage a broad-based information exchange.

The Committee for Conservation has expanded upon this early mandate by providing, in its Triennial Meeting, a forum for the widest possible range of conservation activities. By welcoming contributions from all disciplines within the profession by those active at all levels, students as well as senior specialists, and by encouraging a wide variety of approaches ranging from scientific research to case studies and reports of work in progress, the Triennial Meetings have served to sum up the current state of knowledge in the field as a whole. These features have contributed to a diversity of content and have distinguished the Committee's Triennial Meeting from professional meetings with invited speakers convened to address a single topic.

Through their interim meetings and newsletters, the Working Groups have provided an effective forum for professional exchange and development and for the advancement of knowledge within their disciplines. In order to balance the specialization promoted by Working Group activity with cross-disciplinary awareness, this Triennial Meeting will feature four morning plenary sessions aimed at acquainting conference participants with research and trends of interest to all members of the profession. To this end the Directory Board has organized the Working Groups in four sections and appointed four Moderators to select the plenary papers and arrange the sessions. Papers from each Working Group were selected on the basis of their quality and their interest to conservators, scientists, and curators.

The number of papers published in the Preprints have increased dramatically since they were first produced for the 1975 Triennial Meeting in Venice. Publication costs have made it necessary to restrict the number of papers accepted for future editions by concentrating on those papers that contribute the most useful and original information to the field.

As in the past, the Working Group Coordinators have been responsible for soliciting, screening, and editing papers by authors in their Groups. For this edition, they were also asked to rank them for consideration by a Review Committee consisting of the four Moderators which met at the end of January to select the final contents, based on the Coordinators' recommendations. This new procedure entailed considerable editorial input from Coordinators.

The Review Committee met to consider 200 papers of which 165 were selected for publication. Final selection took into account the need to balance the range of contributions as well as the Coordinators' ranking of papers. The ranking categories are described below:

1. Very good: This category was reserved for papers that report work (treatment, technique, analysis, information, infrastructure, etc.) of significant originality and innovation. It was expected that these papers would make a major contribution to the subject. They would be well written and require little or no revision. They would be of general interest to the conservation profession.
2. Good: This category applied to those papers which, although of high quality, lack the degree of originality and innovation found in the "very good" papers.
3. Acceptable: This category was for papers that lack any special quality or significance and those that have a narrower scope than papers in the above two categories. This category included reports of work in progress, more ordinary case studies or analyses, or creditable papers that required more work.

No paper was rejected without consideration by two or more Moderators. In general, the causes for rejection were these:

1. Insufficient original material
2. Missing, insufficient, or unclear explanation of methods
3. Research too preliminary to warrant publication at this stage
4. Same material published elsewhere
5. Content limited to general statements, lacking specific data or application
6. Faulty argument
7. Content lacks specific application to conservation concerns (e.g., art-historical or material culture subjects that offer no practical application to the field)
8. Disorganized or confused text
9. Failure to observe stipulations outlined in the "Instructions to Authors," particularly those regarding page-length restrictions.

As in the past, allowances have been made for authors writing in a non-native language, particularly those in parts of the world where translation and/or professional editorial assistance is not readily available. In some of these cases, where lack of clarity handicapped otherwise worthy content, the Preprints Editor and the Review Committee supplied extensive revisions.

The results of these new editorial procedures have been positive, though mixed. The Review Committee generally agreed with the Coordinators' evaluations in those cases where Coordinators spent sufficient time reviewing draft manuscripts and arranging revisions before submitting their Working Group papers. The changing needs of future Preprints will inevitably result in additional refinements in the editorial and production procedures. It is hoped that these Preprints have benefitted from the new approach developed for this edition, that they serve the profession well, and that they provide a solid basis for the publication's future development.

David Grattan, Gerry Hedley, Nicholas Stanley Price, and Sue Walston
Moderators, ICOM-CC 90

Kirsten Grimstad, Editor, ICOM-CC 90 PREPRINTS

Introduction

Cette Réunion Triennale du Comité de l'ICOM pour la Conservation marque une évolution nécessaire de sa structure et de ses procédures correspondant à l'effectif croissant de cette organisation et à la participation accrue de ses membres. Ces changements concernent le format de la Réunion Triennale, qui comprend désormais des séances plénières, et la sélection par ses pairs des publications de cette réunion. Bien que proposées par le Conseil de Direction, ces initiatives ne furent mises à exécution que grâce à la coopération des membres du Comité à tous les niveaux.

Dans le but de servir au mieux l'organisation pendant cette période de croissance, il a été jugé important de respecter l'esprit dans lequel les Réunions Triennales du Comité pour la Conservation avaient vu le jour. Le Comité fut fondé à Bruxelles en 1967 afin de regrouper les travaux de deux organisations similaires de l'ICOM qui s'étaient réunies conjointement depuis plus de dix ans : la Commission pour la Conservation des Peintures et le Comité International des Laboratoires de Musées. La Commission pour la Conservation des peintures, qui en fut le précurseur, était composée de directeurs et de conservateurs de musées. Elle fut fondée en 1948 pour centraliser et diffuser les informations sur l'examen, l'enregistrement, le nettoyage et la réparation des peintures, et par suite pour en encourager l'échange au niveau le plus élevé.

Ce mandat initial du Comité pour la Conservation devint, grâce à la Réunion Triennale, un forum pour une gamme d'activités de conservation la plus étendue possible. Accueillant la contribution de tous, étudiants aussi bien que spécialistes confirmés dans toutes les disciplines de la profession, et encourageant une diversification des méthodes, de la recherche scientifique aux cas d'espèce et aux rapports de travaux en cours, les Réunions Triennales ont servi de point focal pour la récapitulation de toutes les connaissances relatives à ce sujet. Ces attributs ont contribué à une grande diversité de contenu et séparent les Réunions Triennales du Comité des séances professionnelles où les présentations données par des conférenciers invités traitent d'un sujet unique.

Les Groupes de Travail ont fourni, par l'intermédiaire de leurs réunions intérimaires et leurs bulletins, un milieu propice aux échanges et aux développements professionnels, ainsi qu'à l'avancement des connaissances propres à leurs disciplines. Dans le but d'équilibrer la spécialisation promue par l'activité des Groupes de Travail avec une prise de conscience interdisciplinaire, la Réunion Triennale comportera quatre matinées plénières au cours desquelles les participants à la conférence pourront se familiariser avec la recherche et les orientations susceptibles d'intéresser tous les membres de la profession. Pour ce

faire, le Conseil de Direction a organisé les Groupes de Travail en quatre sessions et a nommé quatre Modérateurs qui sélectionneront les présentations devant être données lors de la séance plénière et qui organiseront leurs sessions. Pour chaque Groupe de Travail, la sélection des présentations fut basée sur leur qualité et leur intérêt pour les conservateurs, les chercheurs scientifiques, et les restaurateurs.

Le nombre de présentations publiées dans les *Prétirages* a augmenté considérablement depuis leur introduction lors de la Réunion Triennale de Venise en 1975. En raison des frais de publication, les présentations acceptées pour les éditions futures devront être limitées à celles qui offrent les informations les plus utiles et les plus inédites.

Comme par le passé, les Coordinateurs des Groupes de Travail ont été responsables de la sollicitation, de la sélection et de la révision des présentations rédigées par leurs groupes. Pour l'édition présente, ils ont dû également les classer par ordre de mérite avant de les transmettre à un Comité de Lecture composé de quatre Modérateurs. Ces derniers se sont réunis fin janvier pour en choisir le contenu définitif en se basant sur les recommandations des Coordinateurs. Cette nouvelle procédure a occasionné un travail considérable d'édition de la part des Coordinateurs.

Parmi les 200 présentations revues par le Comité de Lecture, 165 furent retenues pour la publication. Le choix final a tenu compte du besoin d'équilibrer la diversité des sujets et du classement des Coordinateurs. Les catégories de classement sont définies comme suit :

1. Très bon: Cette catégorie fut réservée à la présentation de travaux (traitement, technique, analyse, information, infrastructure, etc.) dont l'originalité et la nouveauté sont significatives. Ces présentations devraient apporter une contribution majeure à leurs sujets respectifs. Bien rédigées, elles ne nécessiteraient qu'un minimum de révisions. Elles seraient en outre d'un intérêt général pour la profession.
2. Bon: Cette catégorie s'appliqua aux présentations qui, bien que de haute qualité, ne possèdent pas le degré d'originalité et de nouveauté trouvé dans celles jugées "très bonnes".
3. Acceptable: Cette catégorie fut attribuée aux présentations sans importance particulière ou de portée plus restreinte que celles des deux catégories précédentes. S'y sont trouvés des rapports sur des travaux en cours, des cas d'espèce ou des analyses plus banales ou des présentations dignes d'intérêt mais sujettes à un travail plus approfondi.

Aucune présentation ne fut refusée sans avoir été revue par au moins deux Modérateurs. Les causes de rejet furent en général les suivantes :

1. Insuffisance de matériau original
2. Explication manquante, insuffisante ou peu claire des méthodes
3. Recherche dont la publication serait prématurée à ce stage
4. Matière déjà publiée
5. Contenu limité à des commentaires d'ordre général, dépourvus de faits ou d'applications spécifiques

6. Argumentation défectueuse
7. Contenu dépourvu d'applications scientifiques aux besoins de la conservation (tels que sujets d'histoire de l'art ou de culture matérielle n'offrant pas d'applications pratiques dans leur domaine)
8. Texte mal organisé ou confus
9. Non-observation des conditions indiquées dans les "Instructions aux auteurs," particulièrement en ce qui concerne les limitations de longueur de pages.

Comme par le passé, il a été tenu compte de l'expression dans une langue étrangère, en particulier pour les pays où des services de traduction et/ou d'assistance professionnelle de rédaction ne sont pas facilement disponibles. Dans certains cas où le manque de clarté nuisait à un contenu par ailleurs digne d'intérêt, l'Editeur des Prétirages et le Comité de Lecture ont gracieusement apporté des révisions importantes.

Les résultats de ces nouvelles procédures d'édition furent positifs bien que mitigés. Le Comité de Lecture fut généralement en accord avec l'évaluation des Coordinateurs quand ces derniers avaient pu dévouer un temps suffisant à la lecture des manuscrits préliminaires de leurs Groupes de Travail ainsi qu'à leur révision avant soumission.

L'évolution des exigences des Prétirages futurs donnera sans doute lieu à des raffinements supplémentaires des procédures de rédaction et de production. Il est à espérer que ces Prétirages ont bénéficié de la nouvelle direction prise pour cette édition, qu'ils seront utiles à la profession et qu'ils établiront une base solide pour le futur développement de cette publication.

David Grattan, Gerry Hedley, Nicholas Stanley Price et Sue Walston
Modérateurs, ICOM-CC 90

Kirsten Grimstad, Rédactrice en Chef, Prétirages ICOM-CC 90

Working Group 1

Scientific Examination of Works of Art

Investigation scientifique des oeuvres d'art



ABSTRACT

This is the first comprehensive study of the techniques of one of the most puzzling artists of the 19th century. Neutron induced autoradiography has revealed surprising information regarding the painting techniques of the 19th century American painter, Albert Pinkham Ryder. The emphasis of much of the art historical literature on Ryder focuses on the fact that he was an experimenter who painted in an unorthodox fashion. His notorious reworking of canvases and the thickness of the paint structure can be observed in the autoradiographs and in cross-sections. His brushwork runs the gamut from precise linear renditions to multi-directional expressionist painting. However, this study has shown that he was a more exacting artist than is usually thought making thoughtful changes to achieve a desired effect. Viewed generally as an eccentric, his painting methods demonstrate remarkable control. His keen imagination and sense of color produced striking, carefully-studied results.

KEYWORDS

Autoradiography, Nineteenth Century Painting, Brushstroke, Painting Technique, Albert Pinkham Ryder, Changes

EXAMINING ALBERT PINKHAM RYDER'S PREPARATORY SKETCH AND COMPOSITIONAL CHANGES BY NEUTRON INDUCED AUTORADIOGRAPHY

Ingrid C. Alexander and Jacqueline S. Olin
Conservation Analytical Laboratory
Smithsonian Institution
Washington D.C. 20560 USA

Introduction

The examination of the paintings of Albert Pinkham Ryder (1847-1917), is the first comprehensive study of the materials and techniques of one of the most enigmatic artists of the American 19th century. In addition to the traditional laboratory analyses carried out with x-ray diffraction, x-ray radiography and gas chromatography/mass spectroscopy, neutron induced autoradiography has made some remarkable new discoveries. This technique was first adopted to study nineteenth century American painters in the 1960s.¹ A major study of Rembrandt has also been undertaken as well as works by other artists.²

Neutron induced autoradiography is a non-destructive method of examination. Numerous tests have been carried out to test the effects of radiation on paintings and it was determined that radiation does not effect the stability of the painting.³ Recent studies determined that no changes have occurred in the painting media of samples of paintings activated in the 1960s.⁴

Ryder's technique, largely considered to be experimental, reveals itself to be more thoughtful. The characteristics of his brushstroke have been examined and evidence of the frequent reworking of his canvases has been seen. Since Ryder's paint layers are extraordinarily thick, infrared reflectography did not provide evidence of any underdrawing or preparatory sketch. Some evidence of a preparatory sketch has been discovered by autoradiography. In addition, the various stages of execution have been examined using this technique.

The poor condition of many of his paintings, reported even during his lifetime, caused many canvases to be restored. Loss of detail resulted from the extensive restoration of these paintings. The autoradiographs have revealed some of this lost detail and delicacy in the artist's technique not generally associated with Ryder's painting method. And, sensitivity can be recognized in the underpainting seen in the autoradiographs.

To date, eighteen paintings have been examined by neutron induced autoradiography from the collections of the National Museum of American Art, Smithsonian Institution; Metropolitan Museum of Art and the Phillips Collection.⁵ A series of 12 autoradiographs are taken over a period of two months. The gamma ray emissions are counted by a solid-state detector shortly after activation. Some of the results of the study of Jonah, Christ Appearing to Mary and In the Stable from the collection of the National Museum of American Art are being presented in this paper. These paintings are exemplary of Ryder's style and contain key elements which best describe his working materials and techniques. They date from approximately the mid 1880s.

The scientific examination is being used here to further enhance the art historical studies of Ryder's painters. It cannot be overemphasized that this effort must be made in order to fully utilize the information that is forthcoming from scientific examination.

The activation uses the thermal column of the National Institute of Standards and Technology research reactor. The painting is exposed to a flux of 5×10^9 neutrons/cm²/second for twenty minutes. The film used is Eastman Kodak direct exposure film (DEF).

A Study of Three Paintings

Albert Pinkham Ryder was born in the coastal town of New Bedford, Massachusetts and spent most of his life in New York. He is well known for his landscapes, moonlit seascapes and paintings with mythical and religious themes. He is usually characterized as an eccentric who created coloristic canvases while leading the life of a bohemian. He used his imagination to create his singular visions in his composition. It is documented that he painted in an unconventional way and may have used unsound materials which resulted in severe cracking visible in so many of his paintings.⁶ His working method is primarily considered experimental.

Ryder worked up his canvases to remarkable thicknesses. He apparently was often reluctant to consider his paintings completed and frequently reworked his compositions.

Autoradiography complements the information gathered in x-ray radiography, which reveals the distribution of heavy elements. Lead is observed in x-ray radiography and not in autoradiography. Manganese, which occurs in the earth colors so characteristic of Ryder, activates very well and is responsible for the images early in the series. His restricted palette included other pigments such as Naples yellow and vermilion. Respectively, these contain antimony and mercury which activate and are observable in autoradiography. In addition, gamma ray spectroscopy provided the composition for those elements which were activated. These elements serve as indicators of pigments which are present in the painting such as potassium, which may be associated with Prussian blue since potassium bichromate is used in the manufacture of that pigment (See Table I). Some of the fine details of his painting technique which are often not visible on the surface of the painting, due to their condition, can be seen in the autoradiographs. A richness of execution can be observed particularly in his seascapes where he adopted an exuberant brushstroke.

He began work on Jonah (See fig. 1) in the mid 1880s and worked some ten years on the painting. Through an engraving made of the painting by Elbridge Kingsley and published in 1890, it is known that the painting at one time was quite different in appearance (See fig. 2). The engraving shows that the boat had a mast and tattered sail at one time. Other compositional changes involve the placement of the fish and changes in the figure of Jonah and God. The nature of these changes can be observed at various intervals in the autoradiographs. In autoradiograph 5, taken 3 hours after activation and exposed for 3 hours, a free preparatory sketch of the boat can be seen as well as the artist's agitated brushstrokes (See fig. 3). The artist has used a loaded paintbrush to define the initial contour of the boat. Thick globs of paint are deposited along different areas of this broken line. In this autoradiograph, vestiges of the previous composition are together with alterations made for the present composition. A portrait of a woman (See fig. 3) can be seen at a 90 degree angle to the picture plane in the bow of the boat. The face of the woman is clearly drawn with a delicate linear quality. It is finely painted in a technique not observed in Ryder's work and is not considered to be by him.⁷ Much of the paint manipulation observed in this and other paintings can be seen as dots and dashes which are characteristic of Ryder's working method. In this autoradiograph, the strong rays around God's head are visible. In the earlier composition, shown in autoradiograph 11, Ryder adopted a broad rayonnant that extended much further. The antimony-rich area, associated with Naples yellow, is painted in a thick application (See fig. 4). This autoradiograph, taken 14 days after activation and exposed for 14 days, also reveals a faint image of the whale and a clearer view of the figures in the boat.

Passages of thick color dominate the upper portion of the painting, particularly around the head of God where the artist has altered the broad rays of light to a more restricted, though intense interpretation. The artist's emphasis on the power of the sea has resulted in the elimination of the mast and sail in order to create a more violent composition. The fury of what appears to be "alla prima" brushwork and working out of his composition in stages is apparent in the autoradiographs.

A photomicrograph of a cross-section made from a sample taken from the upper right quadrant at the top of a wave illustrate the thick build-up of paint and the

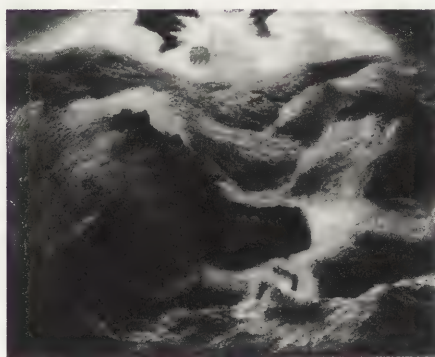


Fig. 1 Jonah, National Museum of American Art, Smithsonian Institution, Washington, D.C.

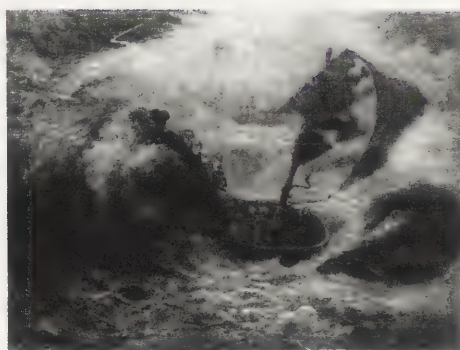


Fig. 2 Elbridge Kingsley wood engraving after Ryder, Jonah, National Museum of American Art, Smithsonian Institution, Washington, D.C.

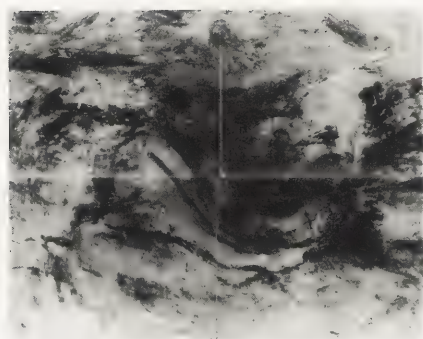


Fig. 3 Jonah, autoradiograph 5

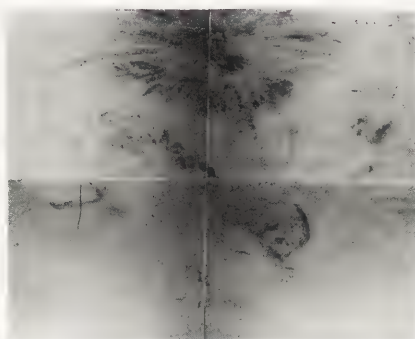


Fig 4 Jonah, autoradiograph 11

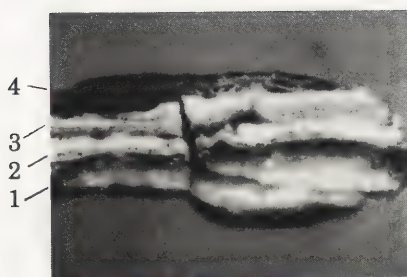


Fig. 5 photomicrograph of cross-section of a sample from the top of wave in upper-right quadrant.

1. ground
2. lead white preparatory layer
3. layer of lead white + red earth
4. varnish

reworking of this area (See fig. 5). Evidence that the artist covered the lower ground with a lead white preparatory layer can be seen in this cross-section.

In Christ Appearing to Mary, (See fig. 6), Ryder has also made some changes in composition. Autoradiograph 6, taken 6 hours after activation for an exposure time of 6 hours, shows a number of alterations and is the most revealing autoradiograph of the series (See fig. 7). The principal changes are: the aureole around the head of Christ has been reduced in its splendor along with the horizon line, which has been heightened, allowing the activity of the figures to dominate the landscape. Thin, very even brushstrokes of the aureole extend down to the horizon line. Also, the artist has changed Christ's gesture of blessing and lowered his left hand.

A very thin line is carefully drawn delineating Christ's arms and hands. The right arm has been changed to appear much thinner and could be related to the story told by Charles Fitzpatrick in his role as a model.⁸ The painting technique of this picture is characteristic of Ryder's smaller works. The usual small jots and dabs of paint are present and there are no rough edges. A blending of the edges of forms is noted frequently in his wet-into-wet technique. Clumps of paint from a loaded brush similar to those observed in *Jonah* can be seen. Horizontal striated brushwork defines the mountain in the background.



Fig. 6 Christ Appearing to Mary, National Museum of American Art, Smithsonian Institution, Washington, D.C.

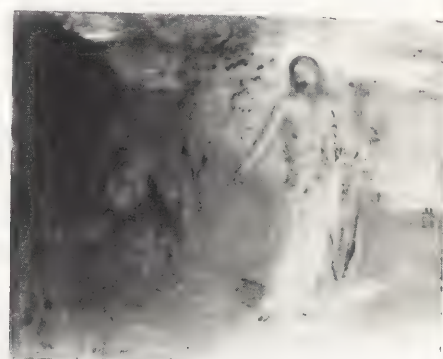


Fig. 7 Christ Appearing to Mary, autoradiograph 6

The same type of careful striations are used in the background of *In the Stable* (See fig. 8). This is seen most clearly in autoradiograph number 5 (See fig. 9). It was taken 3 hours after activation and exposed for 3 hours. Above a smooth ground, which can also be seen in this autoradiograph, Ryder has carefully painted with a brush of medium thickness, the stable background. Once again, there are a number of changes in composition. They occur in the position of the legs of the white horse, as well as in the head of the brown horse. Here, the artist seems to painstakingly position the figures to provide a greater impact as the horses look at one another.

The most noticeable change is in the figure of a man between the two horses. Ryder changed this figure twice before deciding to exclude it from the final composition. In the x-ray radiograph, the figure can be clearly seen sweeping the stable (fig. 10). It is a figure that the artist has used on occasion.⁹ A sleeping dog, excluded from the final execution, is also present in the x-ray radiograph.

In autoradiograph 5, the groom between the horses is carrying a feed bag. He has been replaced with a figure attending to the white horse. The contours of the white horse are executed with broad, sweeping strokes of paint. The artist has created a figure of strength and corporeality. This strength is juxtaposed to delicate passages in the artist's handling of the mane and tail. Some of the lost detail and three-dimensional quality caused by restoration can still be seen in the autoradiographs in the evolutionary stages of the painting process.

A photomicrograph (See fig. 11) of a cross-section from the yellow rooster is a fine illustration of the multi-layered structure associated with Ryder's method of painting. Above the very white manufactured ground, are five layers of red underpaint. Ryder has used this warm priming layer on several occasions to impart a mellow tone to his underpainting. Three layers of brown umber-based color lie just above the priming and this is followed by thin layers of cadmium yellow. These thick paint layers are generally attributed to the artist's constant reworking of an area as well as the experimental nature of his technique in seeking a desired effect.

Conclusion

The autoradiographic study has shown that much of the imagination associated with Ryder's choice of subject matter was at work as he arranged the composition of his paintings. His painting method is shown to be much more thoughtful than is usually attributed to his working style. His smaller easel paintings, for example, have exhibited a calm and studied working method quite unlike the exuberance sometimes adopted in his seascapes.



Fig. 8 *In the Stable*, National Museum of American Art, Smithsonian Institution, Washington, D.C.



Fig. 9 *In the Stable*, autoradiograph 5



Fig. 10 *In the Stable*, x-ray radiograph

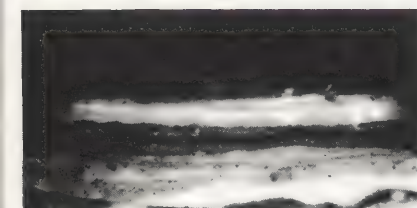


Fig. 11 photomicrograph of cross-section of a sample from the rooster

Table I. Weight Percentages of Elements in Activated Paintings Determined by Gamma Ray Spectroscopy

	Jonah	Christ Appearing to Mary	In the Stable
Elements Associated with Pigments			
Potassium	1.03	0.20	9.35
Calcium	32.60	7.33	N.D.
Chromium	1.14	0.52	0.45
Manganese	0.20	0.14	0.76
Iron	9.65	8.92	8.32
Cobalt	0.25	N.D.	0.01
Zinc	26.07	1.13	16.13
Arsenic	0.56	0.01	0.05
Cadmium	0.02	N.D.	N.D.
Tin	0.002	0.59	0.002
Antimony	0.07	0.016	0.057
Barium	17.94	73.67	3.33
Mercury	1.67	0.57	0.44

Elements Present in Other Materials in the Paint Structure (Medium, Binders, etc.) in Significant Concentrations

Aluminum	3.65	2.85	N.D.
Sodium	2.08	1.51	2.24
Chlorine	1.00	0.69	58.50
Strontium	2.48	1.65	0.15

Elements Present in Trace Quantities

Scandium	0.0001	0.0002	0.0006
Indium	0.0001	0.0001	N.D.
Samarium	N.D.	N.D.	0.001
Gold	0.0004	0.003	0.0016

N.D. Not detected

NOTES

1. M.J. Cotter, P. Meyers, L. van Zelst, C.H. Olin, E.V. Sayre, "A Study of the Materials and Techniques Used by Some XIX Century American Oil Painters by Means of Neutron Activation Autoradiography," in *Applicazione dei metodi nucleari nel campo delle opere d'arte. Atti dei*

- Convegni Lincei, 11 (Rome: Accademia Nazionale dei Lincei, 1976), 163-203.
2. M. Ainsworth, P. Meyers et al in Art and Autoradiography: Insights into the Genesis of Paintings by Rembrandt, Van Dyck and Vermeer (New York: Metropolitan Museum of Art, 1982); J. Kelch, C. Laurenze, K. Slusallek, C.O. Fischer, W. Leuther, "Gemäldeuntersuchung mit Neutronenaktivierungs-Autoradiographie und -Analyse," in Acte du Symposium Zerstörungsfreie Prüfung von Kunstwerken (Berlin, 1987), 95-104; Gerhard Pieh, "Die Restaurierung des 'Mann mit dem Goldhelm'," in Maltechnik Restauro, vol. 1 (1987), 9-34; C.O. Fischer, J. Kelch, C. Laurenze, W. Leuther, K. Slusallek, "Die Neutronen-Aktivierungsanalyse," Restauro, vol. 4 (1988), 259-267.
 3. Ainsworth et al, Art and Autoradiography, 105-110.
 4. J.S. Olin, D.W. Von Endt, Y.T. Cheng and M. Ligeza, "An Examination of Neutron Induced Autoradiography and Gamma Spectroscopy for the Study of Paintings," in Materials Research Society Symposium Proceedings, vol. 123, eds. E. Sayre, P. Vandiver, J. Druzik and C. Stevenson, (Pittsburgh: Materials Research Society, 1988), 33-38.
 5. The autoradiographs are archived at the Conservation Analytical Laboratory, Smithsonian Institution.
 6. Elizabeth Broun, Albert Pinkham Ryder (Washington: Smithsonian Institution Press, 1989), 122-132.
 7. There is a stencil mark of the canvas which reads "prepared by Edward Dechaux/New York." The firm of Dechaux discontinued this style of stencil in 1840 which would provide strong evidence that whoever painted the hidden portrait, probably purchased the canvas around that time.
 8. Fitzpatrick posed for the figure of Christ and remarked to Ryder that he felt he was too muscular to depict a figure who had just been in the grave for three days. Ryder may have, accordingly, made some adjustments. See Kendell Taylor, "Ryder Remembered," in Archives of American Art Journal, 24, no. 3 (1984): 9.
 9. A lone stable groom is sweeping in Ryder's The Stable in Vassar College Art Gallery, Poughkeepsie, New York.

ABSTRACT

Pyrolysis-gas chromatography was used for identification of natural gum types (gum, arabic, ghatti, guar, karaya, and tragacanth). Regardless of chemical and structural similarities between different gum types, the identification of gum based on manual or computer aided pyrogram matching of peak and intensity patterns is possible.

Identification of gums is feasible from samples as small as 1 μ g. Pyrolysis at lower temperatures (400°C) provide a better match between analytical results obtained from analysis of pure gums and gum-pigment mixtures.

KEYWORDS

Natural Gums, Pyrolysis-Gas Chromatography

IDENTIFICATION OF NATURAL GUMS IN WORKS OF ART USING PYROLYSIS-GAS CHROMATOGRAPHY

Michele R. Derrick and Dusan C. Stulik
Getty Conservation Institute
4503 Glencoe Avenue
Marina del Rey, CA 90292
U.S.A.

Introduction

Identification of binding media in samples taken from easel paintings, watercolors, pastels, illuminated manuscripts, polychrome sculptures, ethnographical artifacts and wall paintings may answer important questions related to authentication, provenance and artist techniques. This requires not only the classification of a binding medium (oil, egg, gum, resin or wax), but also detailed characterization of a medium type. In the case of natural gums, this means finding out what kind of gum was used (arabic, tragacanth, ghatti, for example).

Several analytical techniques have been used for gum identification. Most of these techniques, except for infrared spectroscopy (1,2), are based on chromatographic separation: TLC, GC, HPLC and GC-MS (3). Classical chromatographic procedures for the characterization and identification of gums are complex and generally require several time-consuming analytical steps. A typical procedure involves acid hydrolysis of the polysaccharide chain, derivatization of individual monosaccharides, followed by suitable chromatographic separation and detection. However, one method, pyrolysis-gas chromatography (PY-GC), allows fast and reproducible characterization of samples containing natural gum without elaborate sample preparation. Another advantage of the PY-GC method is that it needs only a microscopic amount of a sample. A comprehensive review on the application of analytical pyrolysis to problems in art and archaeology has been published recently (4).

Pyrolysis-GC methods have been successfully applied to classify binding media samples as either an oil, wax, egg, resin, glue or gum (5-7). Pyrolysis-GC can also be used to readily distinguish between several types of natural resins (8,9). Only the work of Wright and Wheals (10), using pyrolysis in combination with mass spectrometry, has examined the differences in a variety of natural gums in identification of materials in ancient Egyptian mummy cases.

More studies have been published on PY-GC, PY-MS and PY-GC-MS application for characterization of biologically and biochemically important mono; oligo; and polysaccharides (11-17). These experiments have shown that under optimum conditions of pyrolysis the polysaccharides depolymerize by a transglycosidation reaction forming stable anhydro sugars (11). Fingerprint pyrograms of decomposition products have shown that PY-GC can be used even for analysis of more complex heterosaccharides and polysaccharides-based natural products (18).

This paper describes the use of pyrolysis-gas chromatography (PY-GC) for identification of different types of natural gums.

Experimental

A combination of the CDS Model 120 (Chemical Data System, Oxford, PA) pyroprobe with the HP model 5890 (Hewlett-Packard Co., Avondale, PA) gas chromatograph was used in this study.

The gum samples, usually powders, were placed inside of small quartz sample tubes with plugs of quartz wool on each end and pyrolyzed using a coil type probe. A pyrolysis temperature of 700°C was chosen for analysis of standard gum samples. The temperature of pyrolysis was lowered for analysis of complex samples. Products of pyrolysis passed through an isothermally heated pyroprobe-GC interface (250°C) into the gas chromatograph. The head of the chromatographic column was cooled to -50°C using liquid nitrogen. Under these conditions the products of pyrolysis were frozen or concentrated in a small plug at the head of the column. This procedure, which is called "cryofocusing", improves the pyrogram resolution, reproducibility and provides substantially higher sensitivity than the typically used split injection technique. During analysis the initial oven

temperature of -50°C was ramped at $5^{\circ}\text{C}/\text{min}$ to 250°C . The initial and final temperatures were held for 2 minutes each. An HP Ultra-2 capillary phenyl methyl silicone coated column (25m, 0.32 mm I.D.) was selected with a helium carrier gas at flow rate of 30 ml/minute and FID (flame ionization) as a detector. A collection of natural gums used during this study were acquired from commercial sources (Polysciences Inc., Wilmington PA; Serva Feinbiochemica, Heidelberg; A.F.Suter & Co., London; and Meer Corp., North Bergen NJ) or from colleagues in other conservation laboratories (Los Angeles County Museum of Art, Los Angeles CA; and Canadian Conservation Institute, Ottawa, Canada). All samples were dissolved in deionized water in an ultrasonic bath for 1 hour, filtered and air dried before analysis.

Results and Discussion

Initial studies indicated that the optimum sample size for PY-GC analysis of natural gums is 20-100 μg . Samples as small as 1 μg and as large as 2mg were analyzed and provided recognizable pyrograms. With large samples peak broadening occurred due to column overloading. Whether the sample was introduced as a film, powder or granules made negligible differences on peak pattern of measured pyrograms.

For natural gums, the variations in the pyrograms due to tree gums and species variations are characteristic. These differences allow the various gum types (arabic, ghatti, guar, karaya or tragacanth) to be readily distinguished (Fig. 1). The general peak pattern in pyrograms of each gum is reproducible regardless of the source of the gum (origin, manufacturing procedures) (Fig. 2). Minor variations in the peak patterns will be further investigated with respect to the tree growing location and conditions. The analysis of multiple samples of different origin for each of the analyzed gums did allow us to use a pattern recognition computer program for gum identification.

For this study a set of 16 different samples of 3 natural gums (arabic, guar, and tragacanth) was prepared and analyzed. For each pyrogram, the peak retention times were sorted according to peak area. Factor analysis technique using Statview program (Abacus Concepts, Inc., Berkely, CA) was then applied to the data set. Figure 3 shows a plot of factor analysis results for our sample set. Clustering of the samples depending on the gum type is clearly visible.

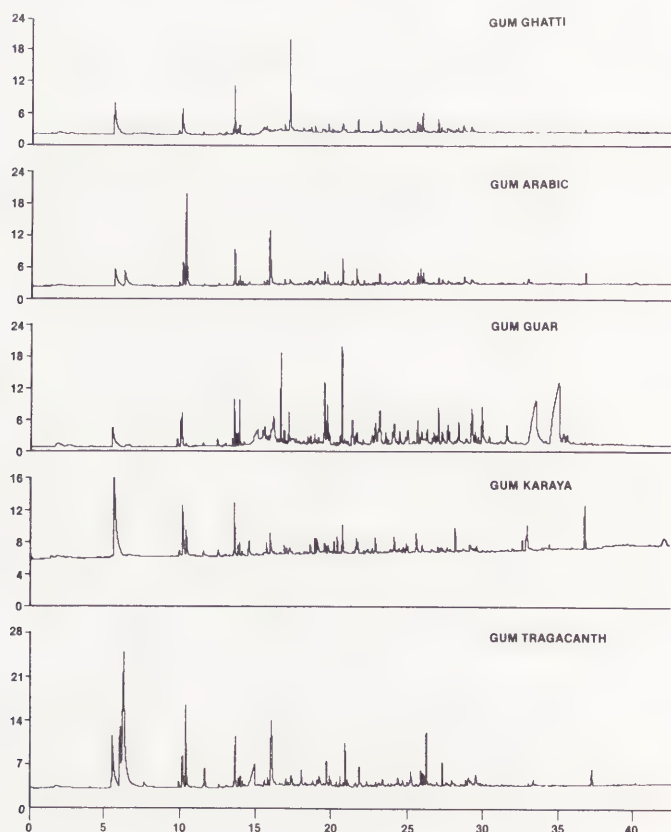


Figure 1. Pyrograms of several types of natural gums.

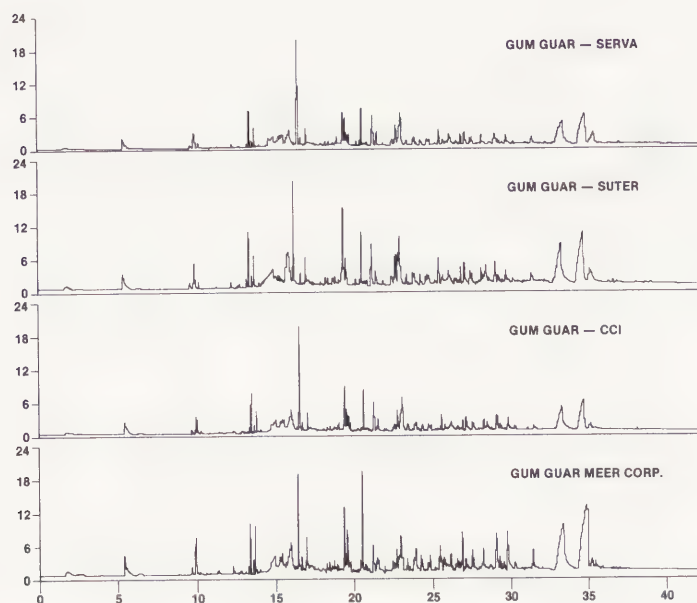


Figure 2. Variation of gum guar pyrogram as a function of gum source.

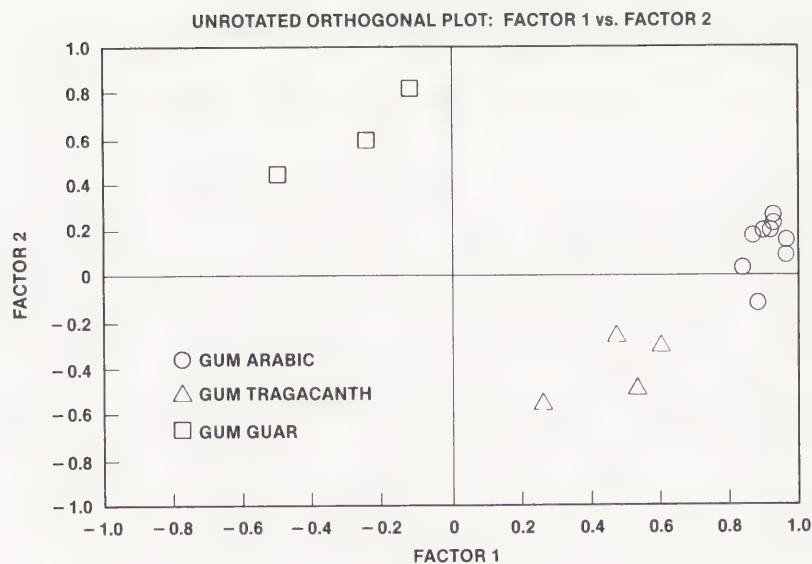


Figure 3. Identification of gums based of factor analysis of measured pyrograms.

Natural gums have been used in art as binding media. As such they are usually found in color layers mixed with inorganic or organic pigments. Analysis of a mixture of gum arabic with ultramarine (Fig. 4a) showed that there is a catalytical effect from pigments during pyrolysis of gum-pigment mixtures which changes peak pattern and peak intensity in the pyrogram. Optimization of experimental conditions during pyrolysis of gum-pigment samples has shown that a lower temperature of pyrolysis decreases the differences between pyrograms of pure gum and gum mixed with a pigment (Fig. 4a,b). Pyrograms recorded at 400°C provide a much better match than pyrograms recorded at 700°C. At the same time, the pyrograms in Figure 5 show that regardless of the pigment type in the sample, the basic and characteristic peak pattern typical for a particular gum is still present and can be used for gum identification.

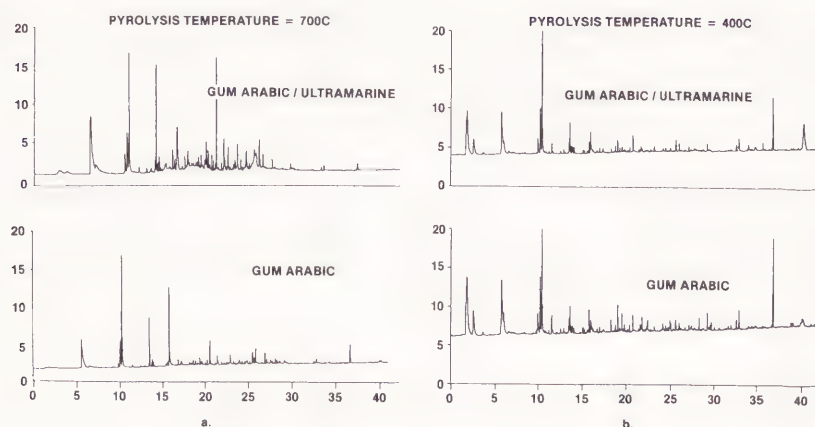


Figure 4. Match between pure gum and gum-pigment mixture as a function of pyrolytic temperature; a-pyrolysis at 700°C; b-pyrolysis at 400°C.

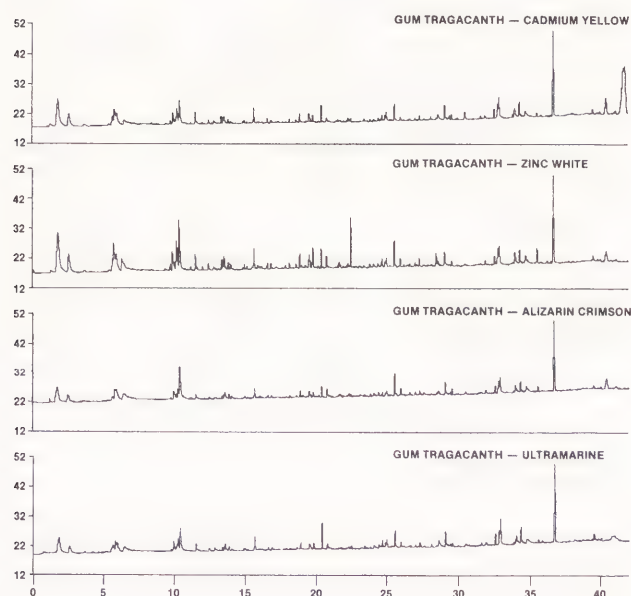


Figure 5. Variation of gum tragacanth pyrogram as a function of pigment type in the sample.

Conclusions

Results of this study have shown that regardless of chemical similarities between different types of natural gums, the identification of the gum type using PY-GC is possible. Pyrograms within a gum type are reproducible and gums of different types show enough differences in peak pattern and peak intensities that manual pyrogram matching or a computer based factor analysis program can be used for successful gum identification.

Optimum sample size for analysis is 20-100 μg but samples as small as 1 μg can also be analyzed directly without elaborate sample preparation. The presence of pigment in the analyzed sample can change the character of the pyrogram. If such problems occur, lowering the pyrolysis temperature can be used to rectify the situation.

Acknowledgements

We are grateful to John Twilley, Los Angeles County Museum of Art, and to Scott Williams, Canadian Conservation Institute, for allowing us to sample their natural gum reference collections.

Bibliography

1. L. Masschelein-Kleiner, J. Heylen and F. Tricot - Marcx, Contribution à l'analyse des liants, adhésifs et vernis anciens, Studies in Conservation, 13 (1968): 105-121.
2. M.R. Derrick and D.C. Stulik, to be published.
3. L. Masschelein-Kleiner, Analysis of paint media, varnishes and adhesives, R. Van Schoute and H. Verougstraete-Marco Eols. Chapter X in Scientific Examination of Easel Paintings, PACT No. 13, Strasbourg (1986): 185-207.
4. A.M. Shedrinsky, T.P. Wampler, N. Indictor and N.S. Baer, Application of Analytical Pyrolysis to Problems in Art and Archaeology: A Review, Journal of Analytical and Applied Pyrolysis, 15 (1989): 393-412.
5. N. Stolow and G. deW. Rogers, "Further Studies by Gas Chromatography and pyrolysis techniques to Establish Ageing Characteristics of Works of Art", Application of Science in Examination of Works of Art, W.G.Yong (ed.) (Museum of Fine Arts, Boston, 1973): 223-228.
6. G. deW. Rogers, "An Improved Pyrolytic Technique for the Quantitative Characterization of the Media of Works of Art", Conservation and Restoration of Pictorial Art, N.Brommelle and P.Smith (eds.), (London: Butterworth, 1976): 93-100.
7. T.P.Wampler, S.A.Liebman, E.J.Levy and Z.Barov, "Authentication of Archaeological Specimens by Pyrolysis Capillary Gas Chromatography", Chromatography as a Quality Control Tool, R.B.Huntoon (ed.), (New York: Marcel Dekker, in press).
8. A.M.Shedrinsky, T.P.Wampler and N.S.Baer, "The Identification of Dammar, Mastic, Sandarac and Copals by Pyrolysis Gas Chromatography", Weiner Beridate, 5, no.4, in press.
9. K.Kakiura, A.Yamaji and H.Yuki, "Analysis of Natural Resins by Pyrolysis Gas Chromatography. I. Classification of Natural Resins by Pyrograms", J. Pharm. Soc.Japan, 93, no.6 (1973): 769-775.
10. M.M. Wright and B.B. Wheals, Pyrolysis - mass spectrometry of natural gums, resins and waxes and its use for detecting such materials in ancient Egyptian mummy cases (cartonnages), Journal of Analytical and Applied Pyrolysis, 11, (1987): 195-211.
11. R.J. Helleur, Characterization of the Saccharide Composition of Heteropolysaccharides by Pyrolysis -Capillary Chromatography - Mass Spectrometry, Journal of Analytical and Applied Pyrolysis, 11 (1987): 297-311.
12. D.R. Budgell, E.R. Hayes and R.J. Helleur, Direct identification of pentoses and hexoses by pyrolysis capillary gas chromatography, Analytica Chimica Acta, 192, No. 2 (1987): 243-253.
13. S.L. Morgan and A. Jacques, Characterization of simple carbohydrate structure by glass capillary pyrolysis gas chromatography, Analytical Chemistry, 53 (1982): 741-747.
14. A. Van der Kaaden, J. Haverkamp, J.J. Boon and J.W. De Leeuw, Analytical pyrolysis of carbohydrates. I: Chemical interpretation of matrix influences on pyrolysis mass spectra of amylose using pyrolysis -gas chromatography - mass spectrometry, Journal of Analytical and Applied Pyrolysis, 5 (1983): 199-220.
15. A.Van der Kaaden, J.J. Boon and J. Haverkam, The analytical pyrolysis of carbohydrates 2, Differentiation of homopolyhexoses according to their linkage type, by pyrolysis - mass spectrometry and pyrolysis - gas chromatography - mass spectrometry, Biomedical Mass Spectrometry, 11 (1984): 486-492.
16. R.J. Helleur, Characterization of the saccharide composition of heteropolysaccharides by pyrolysis - capillary gas chromatography-mass spectrometry, Journal of Analytical and Applied Pyrolysis, 11 (1987): 297-311.
17. R.J. Helleur, D.R. Pudgell, E.R. Hayes, Identification of the composition of oligosaccharides and polysaccharides by pyrolysis - capillary gas chromatography, Analytical Chimica Acta, 192 (1987): 367-372.
18. P.Feng and G.D.McGinnis, "Thermal Fragmentation for the Identification of Pyrolytic Products from Bark Polysaccharides", Anal. Chem., 53, No.14 (1981): 2172-2174.

ABSTRACT

The authors have conducted microscopic studies in natural and fluorescent light on three pieces by the great 19th century Hungarian painter, Mihály Munkácsy dating from the period characterised by the use of asphaltum.

The aim of the investigations was to observe the marks of deterioration, the techniques and materials used by the artist. In order to define the media the cross sections were stained.

According to the results Munkácsy used oil and resin as media on these pieces, most of the time a mixture of the two. The darkening of the pictures may not merely be due to the diffusion of an originally dark material from one layer to another but is facilitated by the transformation and darkening of the components within the same layers.

KEYWORDS

19th century, darkened painting, light and fluorescent microscopy, cross sections.

MICROSCOPIC INVESTIGATIONS OF 19th CENTURY DARKENED PAINTING SAMPLES

Klara Erdőhalmi-Török and Marta Kissné Bendefy
Conservation Department
National Centre of Museums
1087. Budapest
Könyves K. krt. 40.
Hungary

Introduction

One of the most characteristic painters of 19th century Hungarian art was Mihály Munkácsy (1844-1900) who studied painting in Vienna, Munich and Dusseldorf and then worked in Paris for a long time.

A large number of his pieces in the Hungarian National Gallery have been badly damaged. The damages included darkening - at times to the degree of making certain details disappear -; dull patches near the bright parts; and the emergence of uneven surfaces (reliefs, crackles). These phenomena can be observed on pieces painted in a 9-year-period (see Fig. 1). Similar damages have occurred on the paintings of most of his contemporaries, all in connection with a special painting technique characterised by the use of materials containing asphaltum or bitumen.

In order to prevent further damages and to find the adequate procedure of conservation/restoration the National Gallery launched a complex project involving other institutions as well, the first step of which was the analytical survey of the materials used by the artist.

Our paper is intended to relate the results of the microscopic analysis of the samples taken from three paintings so far.

Experimental

The samples have first been all photographed under a small-scale microscope then embedded in polyester synthetic resin (Polyol PS 230) and after polishing them we examined in their cross-sections, the composition of each layer as well as the media used by the artist. The cross-sections have been examined by a fluorescent microscope as well and by virtue of this method we managed to make the different layers visible even in some completely dark samples.

The dark mass, usually referred to as asphaltum, has been found in all the samples taken from the three pieces, in the ground as well as in the layers of paint; under the microscope, however, these dark patches seemed not at all uniform in colour or in granulation. This is well-represented in the sample taken from the red carpet of "The Studio" (see Fig. 2). The cross-sections of the other samples taken from other darkened patches of the same painting seem completely dark in natural light apart from the white layer of the ground. The photos taken under the fluorescent microscope, on the other hand, reveal that these apparently uniform cross-sections are divided into layers distinguishable by the different composition or concentration of the materials (see Fig. 3, 4, 5).

The same applies to "Taking Leave".

In the samples taken from "The portrait of the Artist's Wife" the white ground is missing, the artist painted it directly on the panel. A lot of these samples which looked just as the ones taken from "The Studio" or "Taking Leave" were in fact different in their cross-sections. The lowest layer contained a lot of red pigment (see Fig. 7). Another important observation was that a lot of the samples seemed to testify that the dark layer of the surface could not come from the ground by diffusion, as was supposed earlier, since under the dark surface there were clearly distinguishable light layers. According to our analyses the darkening is the result of the transformation and darkening of the components of the given layer.

Darkening because of sulphidization - that is, the sulphur content of the air - has been dismissed on the ground that a lot of the samples revealed darkening not merely on the surface but also under the lighter layers enclosed (see Fig. 6).

During the structural analysis we have observed that not only the surface but also the inside and the back of the samples contain transparent varnish (see Fig. 8, 9). These internal layers, especially in the samples taken from "The Portrait of the Artist's Wife" are relatively thick.

A lot of the samples have been observed to contain a layer of fine grains under the layer of varnish on the surface (see Fig. 9). This layer has been supposedly applied by the painter himself in order to tone down the bright



Fig. 1 "Portrait of the artist's wife"

colours. According to the fluorescent photos these grains are original components of the present layer and have not come there from the ground by diffusion or floating. This hypothesis has been supported also by the fact that we have found a clearly distinguishable, transparent, clear layer of varnish under the granulated surface (see Fig. 8).

A lot of the samples taken from "The Portrait of the Artist's Wife" reveal a crinkled layer of the same grains under the thin layer of varnish on the surface (see Fig. 9). The surface of these samples seemed dull and slightly crinkled even before having been embedded (see Fig. 10).

The analysis of the media used in the samples has been conducted by staining the cross-sections. The microscopic staining of the cross-sections and the organic analytical procedures by high-precision instruments complement each other well since the microscopic method enables the analyser to co-ordinate the types of media (protein, oil, resin) to the corresponding layers, while by the instrumental procedures a more precise definition (glue, linseed oil, mastic, etc.) is possible.

The results of the abovementioned tests can be summarized as follows:

- in the white ground staining by Sudanblack B solution revealed oil;
- in the layers of varnish in the samples of all the three paintings contain oil as well as resin (by Sudanblack B and Bromocresol purple Solutions);
- both the dark layers of the ground and those of paint contain oil and resin except for the samples taken from the skin-colour which are all in good condition having contained merely oil and no resin.

Conclusion

According to the observation the dark layers can be found in all the three paintings but are of different characters. The darkening of the pictures may not merely be due to the diffusion of an originally dark material from one layer to another but is facilitated by the transformation and darkening of the components within the same layers.

Several times there were observed pigment grains in the dark layers (primarily red pigment).

In the samples taken from the parts in bad condition there were thin layers of varnish between the layers of paint as well as on the surface.

Munkácsy used oil and resin as media on these pieces, most of the time a mixture of the two. In the parts preserved in good condition he used oil exclusively.

References

- Althöfer, H.: Das 19. Jahrhundert und die Restaurierung. Beiträge zur Malerei, Maltechnik und Konservierung, Callwey, München 1987.
- van Asperen de Boer, J.R.J.: Some practical aspects of the preparation and study of cross sections, ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen 1984.
- Balló, E.: Az olajfestés mestersége (The craft of oil painting) Ed. by the writer, Budapest, 1918.
- Bergeon, S.: Painting technique: priming, coloured paint film and varnish, PACT, 13. Strasbourg 1986.
- Delburgo, S. J.-P, Rioux et E. Martin: Étude analytique de la matière, Laboratoire de Recherche des Musées de France, Annales 1975.
- Delburgo, S.: Les alterations de la couche picturale sous l'objectif du microscope, Laboratoire de Recherche des Musées de France, Annales 1975.
- Gettens, R.J. and Stout, G.L.: Painting materials, A short encyclopaedia, Dover Publications, New York, 1966.
- De Keijzer, M.: The preparation and the examination of paint cross section, applied to paintings by Vilmos Huszár, Fifth International Restorer Seminar, Veszprém, 1986.
- Masschelein-Kleiner, L.: Ancient binding media, varnishes and adhesives, ICCROM, Rome, 1985.
- Masschelein-Kleiner, L.: Analyses of painting media, varnishes and adhesives, PACT, 13. Strasbourg 1986.
- Pozsgai, L., Erdőhalmi-Török, K.: Electron beam microanalytical examination of samples from the painting "Studio" by Mihály Munkácsy. 2nd International Conference on Nondestructive Testing, Microanalytical Methods and Environment

Evaluation for Study and Conservation of Works of Art, Perugia, 1988.
 Wittmann, Zs., Bélafi-Réti K., Décsy, Z., Erdőhalmi-Török, K., Kiss-Bendefy, M., Vassányi I., Velledtis L.: Examination of painting materials used by Mihály Munkácsy for his painting "Studio". Archaeometric Research in Hungary, National Centre of Museums, 1988.

Zimmerman, B.: Systematische Untersuchungen zur Anwendbarkeit histochemischer Farbmethode für die Identifizierung von Proteinen und getrockneten Ölen als Bindemittel in Historischen Malmaterialien, Diplomarbeit, Akademie der Bildenden Künste, Dresden, 1984.

Acknowledgement

The authors thank the valuable help of Dr. Gerhard Banik (Österreichische Nationalbibliothek, Wien) and Dr. Dezső Szabó (Experimental Medical Research Institute, Budapest) for their work.

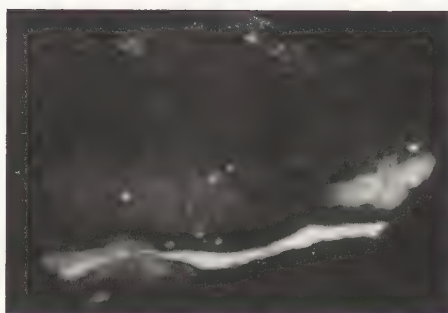


Fig. 2 "Studio". Sample cross section from a relatively good conditioned part

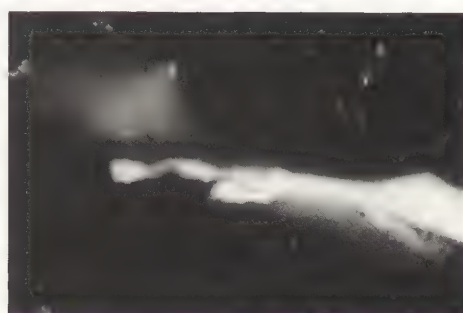


Fig. 3 "Studio". Sample cross section from a darkened part

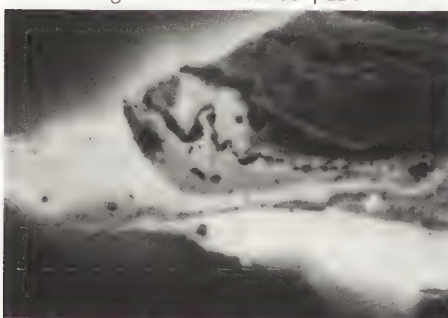


Fig. 4 The previous sample in fluorescent light

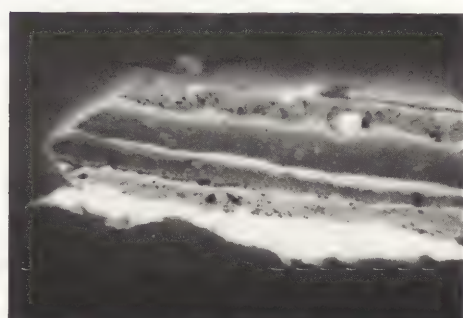


Fig. 5 Sample from another darkened part in fluorescent light

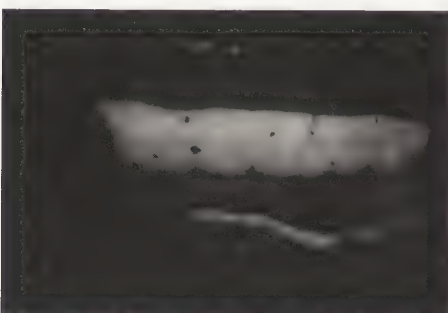


Fig. 6 Sample from a darkened part, there can be seen that not the whole cross section is darkened

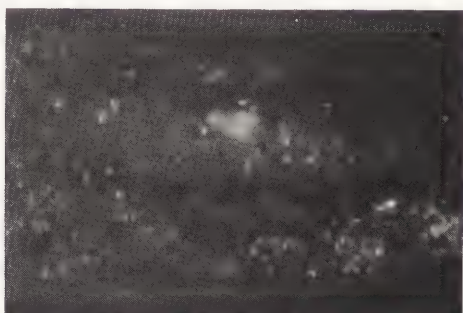


Fig. 7 Sample cross section from the background of the painting "Portrait of the artist's wife"

Fig. 8

Sample cross section from the background of the painting "Portrait of the artist's wife" in fluorescent light

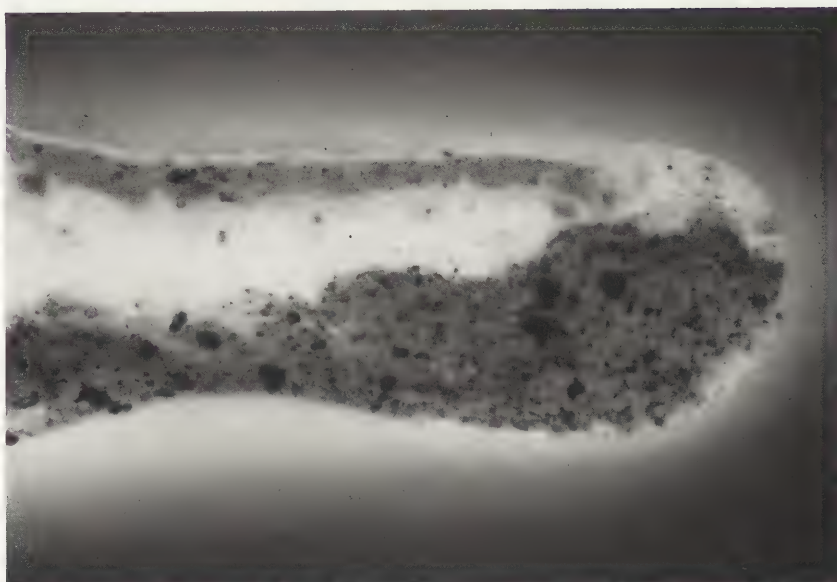


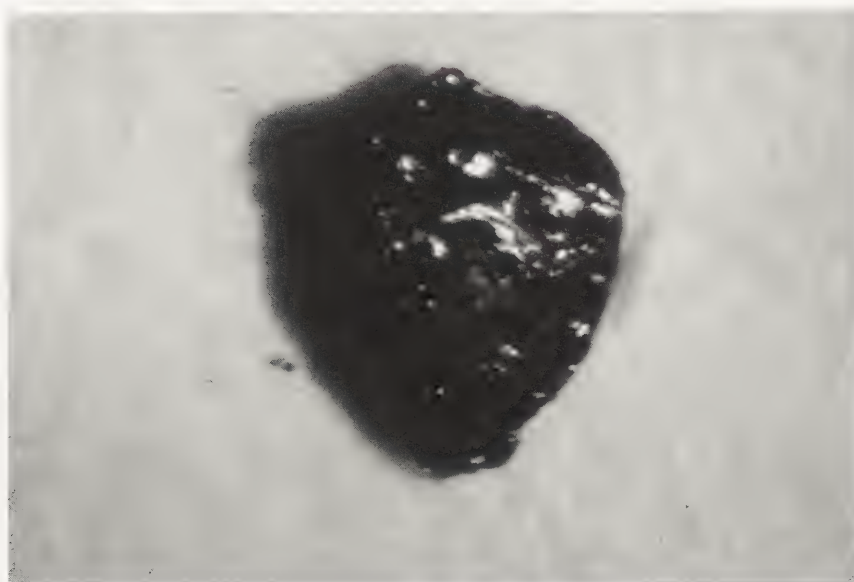
Fig. 9

Sample cross section from the "Portrait of the artist's wife", in fluorescent light, on which can be seen well the grainy layer and crinkling



Fig. 10

The previous sample before embedding



RESUME

Cette étude menée dans le cadre d'une recherche coopérative relate les premiers éléments illustrant la dégradation des émaux peints limousins de la fin du XVe siècle et du début du XVIe siècle. Les plaques analysées ont été minutieusement photographiées assurant le suivi de l'évolution de l'altération. Plusieurs techniques d'émaillage ont pu être identifiées. Afin de comprendre les causes de la dégradation qui semble n'apparaître que sur certaines couleurs des émaux limousins de cette époque, plusieurs méthodes d'analyse complémentaires ont été utilisées. Outre la nature des agents colorants, la matière vitreuse présente des variations de composition d'une couleur à l'autre. La teneur en alcalin des zones altérées diminue en surface fragilisant le verre.

MOTS CLES

Limoges, plaque émaillée, verre, altération, spectrophotométrie d'absorption UV visible, microfluorescence X, microscope électronique à balayage, PIXE.

ETUDE DE L'ALTERATION D'UNE PLAQUE EMAILLEE ATTRIBUEE A LA PRODUCTION DE LIMOGES

Myriam Eveno, Dominique Fromageot, Bruce Kusko et Christian Lahanier
Laboratoire de Recherche des Musées de France
Palais du Louvre
75041 PARIS Cedex 01
FRANCE

Introduction

Pour faire face à l'altération des émaux peints limousins de la fin du XVème siècle et du début du XVIème siècle, un groupe de travail a été constitué dans le cadre de la Direction des Musées de France pour établir un inventaire photographique des objets de cette époque et de cette origine conservés en France et simultanément procéder à leur étude en laboratoire, lors de restaurations d'urgence.

L'exemple retenu est une nativité, conservée au département des objets d'art du musée du Louvre (inv. OA R 359), estimée de la première moitié du XVIème siècle (fig.1). On reconnaît au premier plan, la Vierge, un ange et saint Joseph priant devant l'enfant nu posé sur un pan de manteau de sa mère. Au second plan, une grange et trois bergers referment la composition semi-circulaire. Bethléem se profile dans le fond. Un ange tenant un phylactère se détache sur un ciel étoilé.

Un examen minutieux de la surface a permis de relever son état de conservation. Toute la partie supérieure est craquelée. Les plages bleues, violettes, vertes et lie de vin sont altérées. En particulier l'émail bleu, violet et quelques plages vertes ont perdu leur transparence et leur couleur en surface (fig. 2 et 3). Quelques écailles ont été transmises au Laboratoire de Recherche des Musées de France qui a établi un protocole expérimental pour l'étude de cet émail.

Examen de la surface de l'émail

L'émail est protégé par un cadre en bois (largeur : 0,17 m, hauteur : 0,2 m). Les bords de la plaque de cuivre sont légèrement incurvés.

L'examen sous éclairage ultra-violet ne révèle aucune différence de fluorescence qui pourrait correspondre à des restes d'adhésif.

L'examen à la loupe binoculaire permet de décrire la technique de fabrication de cet émail (fig.4). Côté revers la plaque de cuivre est couverte d'un contre émail opaque. Aucune inscription n'a pu être décelée. Oxydée côté face (cuprite rouge), elle est couverte d'une couche uniforme de verre pourpre que l'on retrouve sur toutes les écailles. Celle-ci est couverte d'une couche de verre blanc et opaque, présente aussi sur toutes les coupes stratigraphiques. La transparence de cet émail obtenue par amincissement de son épaisseur avant cuisson, permet d'ombrer les visages au moyen de la couche pourpre sous-jacente. Un dessin noir est peint sur la couche blanche formant les contours et les



Fig.2 : détail de la Vierge



Fig.1 : La Nativité
(émail peint sur cuivre)



Fig.7 : Point d'analyse par MFX (chiffres) et par PIXE (lettres) et origine des écailles (X)



Fig.3 : détail de Joseph

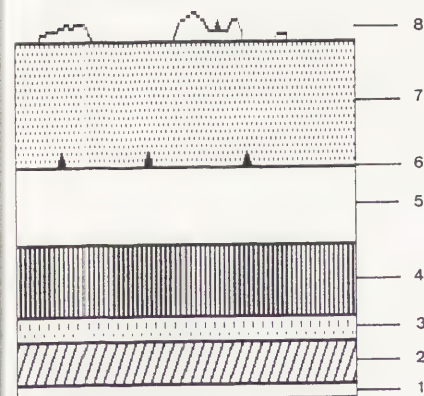


Fig.4 : Stratigraphie de la plaque émaillée

- 1 - contre-émail
- 2 - plaque de cuivre
- 3 - cuprite
- 4 - verre pourpre
- 5 - verre blanc
- 6 - dessin noir
- 7 - verre coloré
- 8 - rehauts blancs, dorure

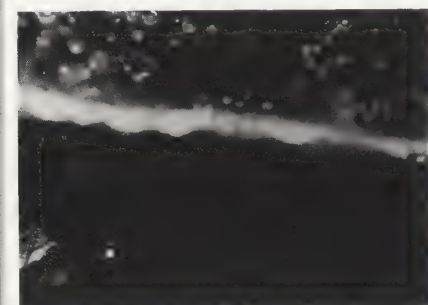


Fig.5 : Coupe au microscope optique (couche pourpre, blanche et verte)

traits des personnages, de l'architecture, et du paysage. Il sert à la mise en place de la composition de l'émail ou à border les formes terminées. On note la présence de début d'altération à l'emplacement de ce trait noir, en particulier dans les yeux et les mains des personnages. Des aplats de verres colorés et transparents sont ensuite peints sur l'émail blanc laissant apparaître le dessin noir (bleu, violet, vert, lie de vin, brun, et beige). Des décors de surface sont appliqués en dernier lieu :

- dorure dont les motifs ne suivent pas toujours les traits du dessin sous-jacent et qui a souvent disparu (par usure) laissant apparaître de minuscules trous dus vraisemblablement à l'emploi d'amalgame ;
- rehauts blancs donnant du relief aux visages ou constituant les moutons dans la prairie ;
- flamme rouge de la bougie de Joseph.

A la différence d'autres plaques étudiées au L.R.M.F., nous n'observons pas ici de paillons d'argent, ni d'enlèvement par scarification à l'épingle du fond blanc opaque permettant de réaliser un dessin aux traits fins par apparition de la couche foncée sous-jacente.

Analyse de la composition des émaux

L'étude en laboratoire des émaux du Moyen-Age nécessite d'opérer directement sur les oeuvres au moyen de techniques non destructives puisque tout prélèvement est défendu. Plusieurs techniques dont la microfluorescence X (MFX), l'émission de rayons X induits par des protons fortement accélérés (PIXE) et la spectrophotométrie d'absorption UV visible permettent d'opérer directement sur la surface de l'oeuvre et apportent des informations complémentaires. Les deux premières donnent l'analyse élémentaire qualitative (MFX) et quantitative (PIXE) de couches superficielles du verre. Les rayons X excitent des zones plus profondes dans l'émail que le flux de protons. De plus, ils excitent plus fortement les éléments de numéros atomiques élevés (raies K). Par contre, dans les deux cas, et d'une manière identique, l'émission de rayons X issus de la matière excitée est absorbée différemment selon la composition chimique du verre et les longueurs d'onde du rayonnement.

La spectrophotométrie d'absorption UV visible a permis de vérifier la valence des agents colorants dans les parties altérées.

La restauration de cet émail a autorisé la mise à disposition d'une dizaine d'écailles au laboratoire. Quatre fragments significatifs, après examen et enregistrement photographique, ont été préparés sous forme de coupes stratigraphiques. Ces fragments correspondent à des plages de verre vert intact (fig. 5) et bleu altéré (fig. 6). Ces coupes ont permis de faire l'analyse quantitative de chacune des couches au microscope électronique à balayage (MEB). Ces résultats quantitatifs, bien que moins nombreux que ceux obtenus par PIXE, sont importants car ils permettent de vérifier la cohérence des analyses effectuées au moyen de l'accélérateur par comparaison à celles obtenues au MEB sur des zones vertes intactes ou bleues altérées de la surface.

Ainsi, l'association de ces méthodes permet d'identifier :

- par PIXE la composition de surface de la totalité des couleurs intactes et celle des produits d'altération des bleus, violets, verts et lie de vin ;
- par l'analyse des coupes, d'avoir celle des couches internes en particulier le pourpre, le blanc opaque ainsi que le bleu non altéré sous-jacent.

Analyse directe par microfluorescence X

L'analyse par microfluorescence X est conduite à l'air sur des plages millimétriques(1). L'excitation est produite à l'aide d'un tube de rayons X à anticathode de molybdène (50kV, 30mA). Le spectre est analysé par le système 5000 ORTEC. 27 points de l'émail (localisés sur la fig.7) ont été analysés afin de caractériser qualitativement les agents colorants. Les éléments légers (fondants et formateurs de réseau) ne peuvent être détectés dans ces conditions expérimentales. Les résultats confirment les données publiées :

- le verre bleu altéré du manteau de la Vierge, de la manche et du col du saint Joseph est coloré par le cobalt (points 3,4, 9 et 21 de la fig.7) ;
- le verre violet altéré de la robe de l'ange et du bas du manteau de la Vierge sous l'enfant est coloré par le cobalt avec une teneur plus élevée en manganèse (points 10, 20 et 27 de la fig. 7) ;
- le verre vert intact du sol et des vallons et coloré par le cuivre en présence de plomb (points 7,8, 18, 19 et 23 de la fig 7) ;
- le verre vert intact du sol et des vallons est coloré par le cuivre en présence de nickel et de cobalt ; ceci permet de penser que le verre original était vert-bleu (points 5 et 6 de la fig. 7) ;

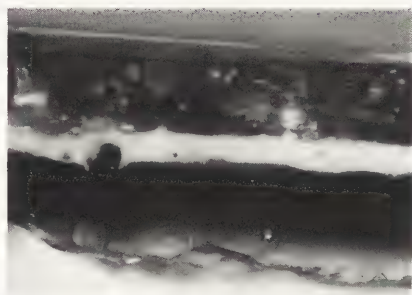


Fig.6 : Coupe au microscope optique (couche pourpre, blanche et bleue)

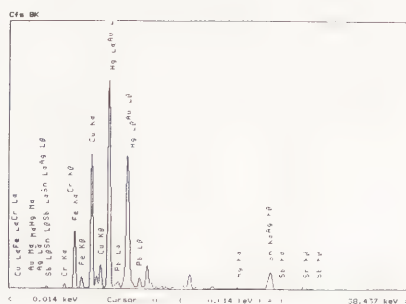


Fig.8 : Spectre de MFX montrant la présence de mercure et d'argent dans la dorure.

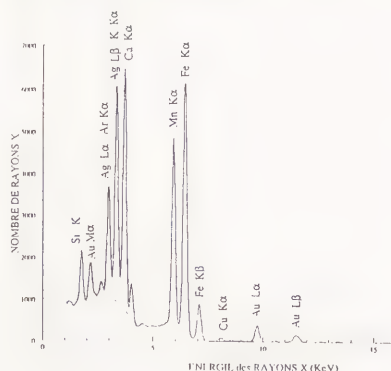


Fig.8 bis : spectre par PIXE de la dorure.

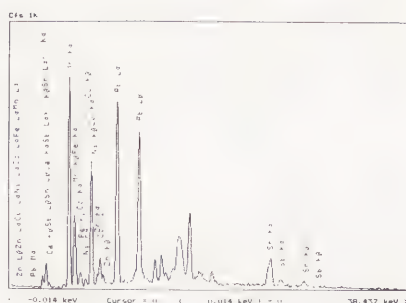


Fig.9 : spectre de MFX montrant la présence de manganèse sur les traits noirs du dessin.

- le verre lie de vin du manteau de saint Joseph et de la robe de la Vierge ainsi que le verre brun de la vache sont colorés principalement par le manganèse en présence de fer (points 1, 2 et 11 de la fig. 7) ;
- le verre beige de l'étable est au contraire coloré par le fer en présence de manganèse (points 12 et 16 de la fig. 7) ;
- le verre opaque blanc des chairs, du bandeau et des moutons contient du plomb comme fondant et de l'étain comme opacifiant (vraisemblablement sous forme de SnO_2), (points 13 et 15 de la fig.7) ;
- la dorure à l'or de la végétation contient de l'argent et du mercure (caractéristique d'une dorure à l'amalgame), (points 17 et 24 de la fig.7) et (fig. 8 et 8 bis) ;
- les traits noirs du dessin contiennent une forte teneur en manganèse (noir de manganèse MnO_2), (points 14 et 22 de la fig.7) et (fig.9).

La présence systématique sur tous les spectres des raies du plomb, de l'étain et de l'antimoine, principalement dans le verre blanc opaque, confirme qu'elles en proviennent. En effet les raies K de ces éléments sont moins absorbées que celles des éléments légers. C'est pourquoi l'analyse quantitative de l'émail par microfluorescence X est erronée puisque le spectre comporte des raies issues de matériaux différents (verres colorés de surface et fond blanc). Elle permet par contre de vérifier que les verres de même couleur ont la même composition et oriente ainsi l'analyse quantitative effectuée par PIXE.

Analyse de coupes au microscope électronique à balayage

Quatre coupes ont été étudiées au MEB JEOL JSM 840 (20 KV Si (Li)). L'image des électrons rétrodiffusés révèle l'homogénéité (hormis quelques bulles) des différentes couches de couleur non altérée (fig.10) et les craquelures dans la couleur bleue altérée (fig.11). Les cartes de répartition chimique (fig.12) montrent la localisation des éléments suivants : Si, Ca, Pb, K, Sn, Na. Elles mettent en évidence la délimitation existante entre le verre bleu intact et sa partie altérée dont l'épaisseur est égale à environ 50 microns. On constate que les concentrations en sodium et potassium diminuent dans le verre altéré alors que celle en silicium augmente. Ces observations globales confirment les analyses quantitatives ponctuelles effectuées sur cette coupe : la concentration en oxyde de sodium diminue fortement de 15 à 2% (tableau 1) alors que la concentration en oxyde de silicium augmente de 71 à 87% dans la zone altérée.

Les analyses multiples effectuées sur les verres pourpres et blancs des quatre coupes montrent que ces verres ont une composition homogène et que l'analyse quantitative au MEB est représentative même sur des plages microscopiques lorsque les concentrations sont supérieures à 0,1% (graphiques 1 et 2).

Fondants

Les compositions des différentes couches colorées sont consignées dans le tableau 1. Les analyses ont été doublées sur chaque couche afin de pallier aux inhomogénéités. On constate que les verres pourpres, bleus non altérés sous-jacents, verts intacts et blancs opaques sont des verres alcalins contenant plus de 20% de Na_2O plus K_2O . Seul le verre blanc opaque contient en plus une forte teneur en oxyde de plomb (16%) et d'étain (21%).

Stabilisants

La teneur en oxyde de calcium varie de 2 à 6% et celle en magnésium de 0,4 à 1,6% valeurs assez faibles mais comparables à celles publiées par Rika Smith, obtenues également au MEB, sur un émail de la suite de Nardon Pénicaud "Christ as Man of Sorrows" (2). De même les concentrations en oxyde d'aluminium voisines de 1,5% sont équivalentes à celles publiées sur l'émail précédent.

Colorants

Les résultats d'analyse confirment les données historiques de la fabrication verrière. (2, 3 et 4).

Le verre bleu non altéré sous-jacent est coloré par le cobalt. Le fer et le manganèse sont en faible teneur comme dans l'émail précédent. Le verre bleu altéré en surface comporte les mêmes teneurs en éléments colorants que le verre bleu sous-jacent. Il en est de même dans l'émail de la suite de Nardon Pénicaud. L'altération ne touche donc pas aux éléments colorants du verre mais en modifie la couleur. Cette différence d'aspect peut provenir de l'état divisé du verre en surface ainsi que des efflorescences.

Le verre vert non altéré est coloré par l'oxyde de cuivre (5%) et l'oxyde de fer (5%). Notons l'absence de plomb présent en général dans les verres verts au cuivre.

Le verre pourpre situé sous la couche opaque blanche est coloré par une teneur élevée en oxyde de manganèse (4%).

Analyse directe par PIXE

L'analyse par PIXE a été effectuée sur AGLAE (Accélérateur Grand Louvre d'Analyses Élémentaires) à l'aide du faisceau extrait. L'énergie du faisceau de protons est égale à 3,2 MeV sur la cible, énergie maximale que l'on peut obtenir actuellement avec cet équipement. Cette énergie a été choisie pour opérer avec la section efficace et la sensibilité les plus élevées pour les éléments chimiques de numéros atomiques supérieurs au calcium ($Z = 20$). Un filtre de 75 micromètres a dû être interposé devant le détecteur de rayons X pour stopper les protons rétrodiffusés. Ce filtre absorbe, de plus, les rayonnements de basse énergie émis par l'émail. Dans ces conditions Na, Mg et Al n'ont pu être détectés.

La profondeur d'émail analysé varie de quelques microns à plusieurs dizaines de microns selon la raie K ou L détectée et l'élément chimique dosé. Par conséquent, l'analyse des plages altérées par PIXE ne donne que la composition du verre altéré dont l'épaisseur est voisine de 50 microns sur la coupe stratigraphique.

L'intensité du faisceau de protons n'a pas été mesurée durant l'analyse de l'émail ; aussi les résultats sont relatifs. Les oxydes ont été dosés stoechiométriquement à partir de standards. Les valeurs de Na_2O , MgO et Al_2O_3 , sont celles obtenues au MEB. Ensuite les concentrations ont été exprimées en pour cent d'oxydes.

Les résultats d'analyse sont consignés dans le tableau 2. Trois verres semblables ont été analysés au MEB et par PIXE. Les compositions obtenues pour le verre vert intact et le verre bleu altéré coïncident parfaitement (tableaux 1 et 2) confirmant ainsi le calcul de l'épaisseur de la couche analysée par PIXE. Celles du verre blanc opaque diffèrent par ces concentrations en étain et en plomb qui sont nettement plus élevées pour les valeurs obtenues au MEB. Les valeurs obtenues par PIXE en étain et en plomb ne se trouvent pas incluses dans l'écart des sept mesures effectuées au MEB.

Les analyses multiples effectuées sur le verre bleu altéré montrent que sa composition est homogène sur des plages millimétriques (graphique 3).

Identification de la valence des agents colorants

La spectrophotométrie UV visible avec sphère d'intégration externe permet d'identifier la valence des éléments colorants du verre, en particulier celle du fer, du manganèse et du cobalt(5) et(6). Les analyses ont été faites directement sur les différentes plages colorées de la plaque émaillée ; les spectres de réflexion obtenus ont été enregistrés sur un spectrophotomètre UV-visible PERKIN ELMER de type lambda 5. L'interprétation des résultats obtenus sur les spectres (fig. 13) sont rassemblés dans le tableau 3. La bande d'absorption dont le maximum est situé à 704 nm correspond à l'ion Cu^{2+} . Les autres maximums d'absorption sont caractéristiques de Mn^{3+} et Co^{2+} . Le manganèse présent dans le verre violet est vraisemblablement sous forme de Mn^{3+} caractérisé par une bande située à 463 nm décelée après déconvolution par transformée de Fourier (fig.13).

Discussion

La convergence des résultats obtenus à l'aide de ces méthodes permet de valider l'utilisation de PIXE pour l'analyse de surface des émaux tant pour les parties altérées qu'intactes.

Nous constatons que les verres les plus riches en potassium, qui pourraient être les plus fragiles, sont en fait les plus stables. Le verre vert intact contient 10% de K_2O et le verre pourpre situé contre la plaque de cuivre mais protégé de l'humidité atmosphérique en comporte 13%. Les autres verres, altérés ou non, en contiennent environ 6%.

En comparant la composition d'un verre intact à celle du même verre altéré en surface, on constate que c'est essentiellement le sodium qui disparaît, trait caractéristique d'une attaque acide (7 et 8).

Le calcul du facteur de stabilité (concentrations exprimées en atomes pour cent des agents formateurs/les agents alcalins) établi par Monsieur Bettembourg, (9), témoigne lorsqu'il est inférieur à 2, de la fragilité de ces matériaux sensibles à l'humidité. L'altération des verres bleus, était prévisible compte tenu de leur composition (facteur de stabilité égal à 1,82). Au contraire, la composition des verres verts correspond bien à celles de verres stables (facteur de stabilité légèrement supérieur à 2). Notons que pour ce dernier la teneur élevée en fer joue le rôle de formateur.

Notons également que la composition d'origine du verre vert-bleu, bien qu'altéré, ne peut être la même que celle du verre vert intact. En effet les teneurs en K_2O et en colorants Fe_2O_3 et CoO sont nettement supérieures (presque doubles) dans la composition du verre intact.

Toutes ces informations ne pouvaient être déduites sans l'intervention simultanée du MEB et d'AGLAE. Nous savons maintenant que la teneur en sodium est

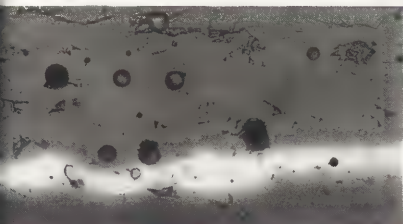


Fig. 10 : image en électrons rétrodiffusés au MEB (couche pourpre blanche et verte).

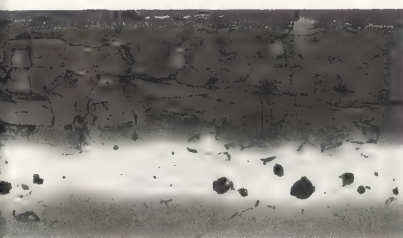
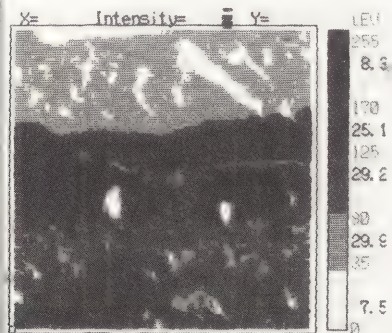
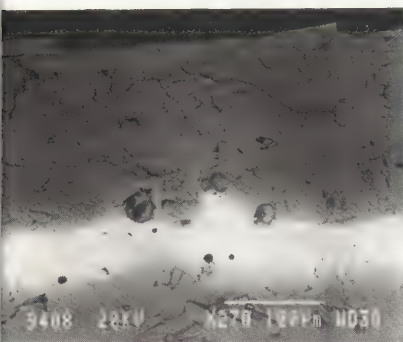


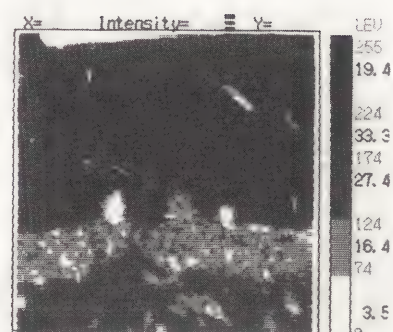
Fig. 11 : image en électrons rétrodiffusés au MEB (couche pourpre blanche et bleue).



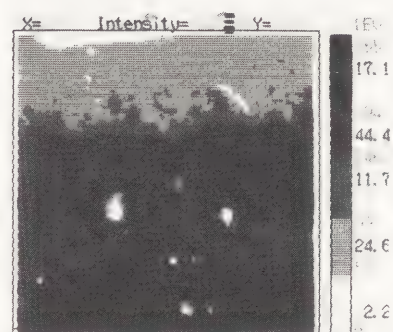
Na

Fig. 12 : image en électrons rétrodiffusés au MEB (couche pourpre blanche et bleue) et cartographie de Na, Si, K, Ca, Pb, Sn.

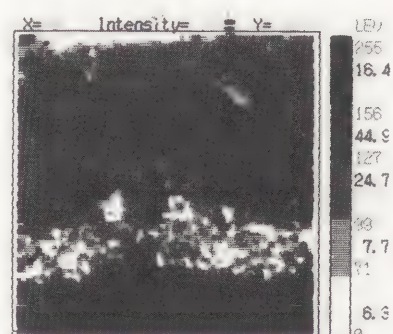
Fig.12 : suite



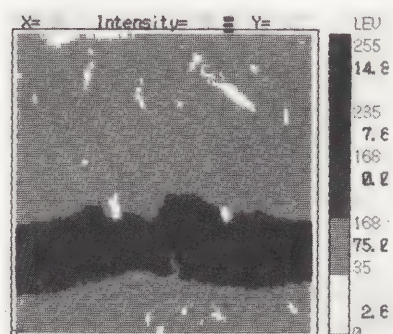
Si



K



Ca



Pb

celle qui varie principalement. La détermination de la composition d'un émail, au moyen de PIXE et de PIGE (pour les éléments légers), permettra de préciser son degré de stabilité, donc de formuler des recommandations préventives

Conclusions

L'étude d'un émail limousin en cours de dégradation a permis, par la mise au point de techniques spectrométriques, d'identifier les causes de l'altération préférentielle de certains verres colorés appliqués sur un même fond.

PIXE, technique nouvelle dans le domaine de la conservation, permet aujourd'hui, au sein du Louvre, de caractériser finement la composition des matériaux et, dans notre cas, de prédire le comportement des émaux. Outre ce caractère préventif, AGLAE révèle la technique des émailleurs de la Renaissance et contribuera certainement à en préciser l'évolution.

Nous remercions A.R. Duval pour sa collaboration à l'étude conduite au MEB sur les coupes stratigraphiques et D. Bagault qui a réalisé la documentation photographique de cet article.

Bibliographie

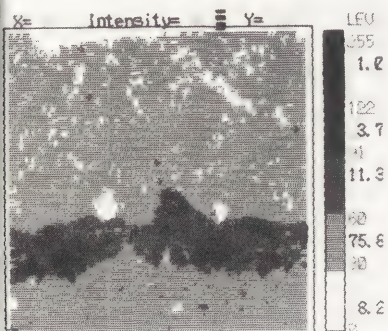
- (1) Christian LAHANIER
L'application des techniques de fluorescence X au Laboratoire de Recherche des Musées de France
International Symposium on the Conservation and Restoration of Cultural Property- Tokyo National Research Institute of Cultural Properties 1979, 135-158
- (2) Rika SMITH, Janice H. CARLSON and Richard M. NEWMAN
Investigation into the deterioration of painted Limoges enamel plaques c. 1470-1530
Studies in Conservation 32 (1987) 102-113
- (3) Peter E. MICHAELS
Technical observations on early painted enamels of Limoges ; their materials, structure, technique and deterioration
The Journal of the Walters Art Gallery vol. XXVII-XXVIII as of 1964-1965
- (4) Maria LUISA Martin ANSON
Revalorización del esmalte en el siglo XIX
Revista Fragmentos núms 15-16 Madrid 1989
- (5) Lorna R. GREEN et F. Alan HART
Color and chemical composition in ancient glass ; an examination of some roman and wealden glass by means of ultra-violet visible IR spectrometry and electron microprobe analysis
Journal of archeological Science 1987, 14, 271-282
- (6) Thomas B. BRILL
Light-its interaction with light and antiquities (1980)
- (7) J. ZARZYCKI
La surface des verres
Verres Réfract. vol. 35 n° 1 janvier-février 1981 pp. 21-30
- (8) J. ZARZYCKI
Le verre et l'eau
Rivista della Staz. Sper. Vetro n° 5 1984 pp 17-28
- (9) J.M. BETTEMBOURG
Composition et altération des verres de vitraux anciens
Verres reflact. vol. 30 n°1 janvier-février 1976 pp.36-42

Oxide	vert intact			bleu intact			bleu altéré			pourpre								Moyenne	blanc							Moyenne	
	1	2	Moyenne	1	2	3	Moyenne	1	2	Moyenne	1	2	3	4	5	6	7		8	1	2	3	4	5	6		7
Na2O	10.9	11.2	11.0	15.5	14.6	16.0	15.4	1.5	3.0	2.2	10.9	7.6	12.5	12.3	10.8	10.6	12.0	12.5	11.2	11.6	12.2	12.4	9.9	10.4	12.4	12.2	11.6
MgO	0.44	0.37	0.40	0.84	0.64	0.58	0.69	0.53	0.30	0.41	1.70	1.20	1.50	1.90	1.70	1.30	1.70	1.80	1.60	1.70	1.50	1.60	1.50	1.30	1.60	1.70	1.50
Al2O3	1.2	1.3	1.2	1.1	1.3	1.2	1.2	0.9	1.3	1.1	1.9	2.4	2.0	2.3	2.3	1.6	3.5	3.7	2.5	2.6	1.9	2.2	1.7	1.6	2.2	2.3	2.0
SiO2	63	63	63	71	72	72	71	89	85	87	60	62	60	59	59	60	58	58	59	36	41	39	37	42	41	39	40
Cl2O	0.43	0.41	0.42	1.40	1.40	1.50	1.40	1.70	1.60	1.60	0.77	0.66	0.58	0.65	0.80	0.75	0.60	0.63	0.68	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
K2O	10.3	11.0	10.6	7.6	7.6	5.5	6.9	3.0	5.2	4.1	14.1	14.2	12.3	12.9	14.7	14.5	12.6	11.9	13.4	4.2	5.0	4.8	6.2	7.5	3.8	4.1	5.2
CaO	2.1	2.0	2.1	1.8	1.8	1.8	1.8	2.3	2.2	2.3	6.0	6.9	6.5	6.1	6.0	6.1	7.8	7.6	6.6	0.15	0.29	0.02	0.38	0.21	0.15	0.17	
MnO	#	#	#	#	#	#	#	#	#	#	4.2	4.3	4.4	4.5	3.9	4.2	3.7	3.8	4.1	0.13	0.08	0.11	0.10	0.05	0.01	0.07	0.07
Fe2O3	5.8	5.4	5.6	0.98	0.90	1.00	0.97	1.3	1.2	1.2	0.50	0.87	0.56	0.37	0.58	0.40	0.54	0.46	0.53	0.06	0.15	0.06	0.20	0.01	0.07	0.05	0.09
CoO	#	#	#	0.16	0.23	0.33	0.20	0.27	0.32	0.290	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#
CuO	5.4	5.1	5.2	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	0.04	0.01	0.08	#	1.30	#	0.23	
SnO2	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	26	18	22	27	19	19	21	21
PbO	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	#	16	18	16	16	15	18	17	17

indique que l'élément est au-dessous de la limite de détection.

Tableau 1 : résultats des analyses par MEB

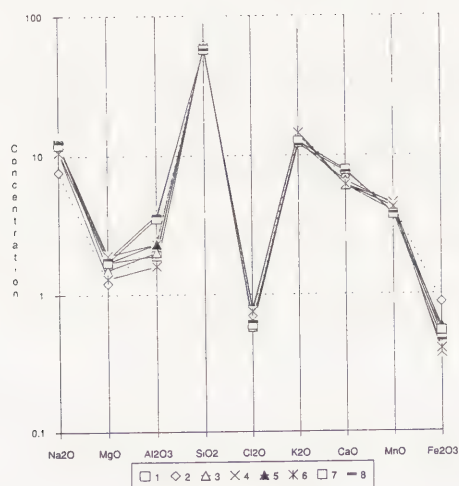
Fig. 12 : suite



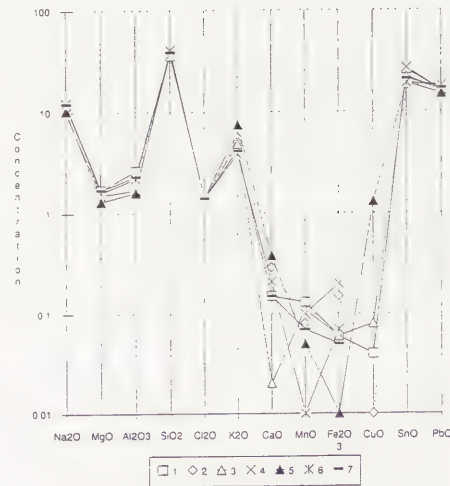
Oxide	vert intact		Moyenne	vert altéré		Moyenne	bleu altéré				Moyenne	violet altéré	blanc	brun	beige	lie de vin			Moyenne	bleu foncé intact
	g	h		e	f		i	j	c	d		k	l	q	o	a	b	n		p
Na2O	118	118		4.0*	4.0*		2.2§	2.2§	2.2§	2.2§		4.0*	11.6§	11*	11*	11*	11*	11*	11*	11*
MgO	0.44§	0.44§		0.50*	0.50*		0.41§	0.41§	0.41§	0.41§		0.50*	1.5§	0.50*	0.50*	0.50*	0.50*	0.50*	0.50*	0.50*
Al2O3	1.2§	1.2§		1.0*	1.0*		1.1§	1.1§	1.1§	1.1§		1.0*	2.0§	1.0*	1.0*	1.0*	1.0*	1.0*	1.0*	1.0*
SiO2	62	63	63	83	81	82	84	86	87	88	87	78	50	70	67	72	74	76	74	59
Cl2O	0.41	0.37	0.39	0.66	0.58	0.62	1.06	0.93	0.85	0.80	0.88	0.55	0.69	0.93	1.12	0.77	#	#	#	0.56
K2O	10.3	10.1	10.2	3.5	4.1	3.8	5.1	4.4	3.4	2.9	3.7	5.7	4.8	5.5	5.8	5.3	4.7	4.1	4.7	14
CaO	2.2	2.0	2.1	2.7	2.6	2.7	3.2	2.7	2.7	2.4	2.7	5.3	0.4	4.6	5.0	4.0	3.9	3.3	3.7	3.2
TiO2	0.044	0.036	0.040	0.026	0.031	0.028	0.037	0.034	0.038	0.035	0.036	0.031	#	0.031	0.044	0.024	0.027	0.015	0.022	0.065
Cr2O3	#	#	#	#	#	#	#	#	#	#	#	0.015	#	#	#	0.033	#	0.010	#	#
MnO	0.15	0.11	0.13	0.10	0.12	0.11	0.15	0.15	0.13	0.11	0.13	2.8	0.06	3.8	3.0	4.5	4.4	3.9	4.3	0.8
Fe2O3	6.1	5.9	6.0	2.5	2.9	2.7	1.4	1.3	1.3	1.2	1.3	0.9	0.049	2.2	5.2	0.2	0.2	0.2	0.2	5.3
CoO	0.041	0.039	0.040	0.17	0.17	0.17	0.30	0.28	0.29	0.28	0.29	0.16	0.0037	0.016	0.032	#	#	#	#	0.048
NiO	#	#	#	0.073	0.069	0.071	0.14	0.13	0.13	0.12	0.13	0.055	0.009	#	#	#	#	#	#	#
CuO	6.1	5.7	5.9	2.0	2.5	2.3	0.65	0.38	0.30	0.24	0.39	0.35	0.077	0.1035	0.049	0.099	0.074	0.063	0.079	5.16
ZnO	#	0.006	#	0.009	0.014	0.011	0.021	0.008	0.010	0.007	0.012	0.029	0.019	0.012	0.001	0.013	0.014	0.007	0.011	0.013
Pb2O	0.008	0.004	0.006	0.007	0.005	0.006	#	0.002	0.002	0.003	#	#	#	#	#	#	#	#	#	#
SiO	#	#	#	0.010	0.006	0.008	#	0.012	0.012	#	#	0.027	#	0.037	0.043	0.053	0.038	0.035	0.042	0.016
MoO	#	#	#	0.009	0.007	0.008	0.017	0.018	0.020	0.011	0.017	0.011	#	#	#	#	#	#	#	#
SnO2	#	#	#	#	#	#	#	#	#	#	#	#	16.4	#	#	#	#	#	#	#
PbO	0.079	0.067	0.073	0.058	0.050	0.054	0.061	0.189	0.041	0.036	0.082	0.40	12.4	0.18	0.18	0.039	0.120	0.031	0.063	0.21

Indique que l'élément est au-dessous de la limite de détection.
§ Résultats pour Na2O, MgO, et Al2O3 pris au MEB.
* Valeur supposée.

Tableau 2 : résultats des analyses par PIXE



Graphique 1 : composition chimique des plages de verre pourpre analysées au MEB.



Graphique 2 : composition chimique des plages de verre blanc analysées au MEB.

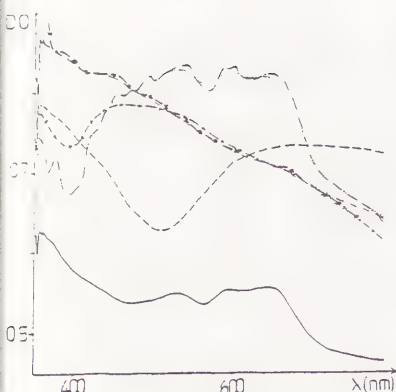
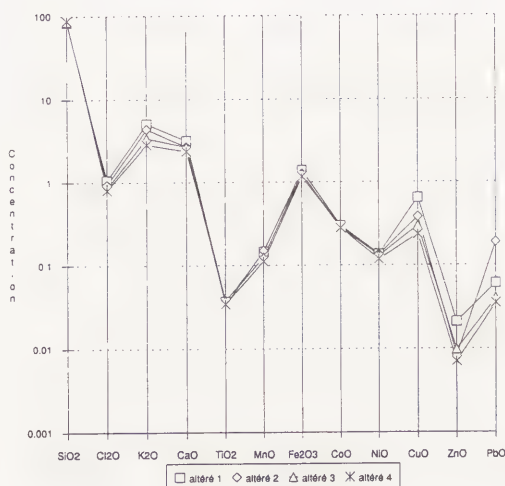


Fig. 13 : spectres d'absorption des agents colorants

— : bleu altéré
- - : vert intact
... : violet
- + : lie de vin
- : beige
- - : idem violet après déconvolution
- * : idem beige après déconvolution

plage analysée	maximum d'absorption	nature de l'ion
vert intact	704 nm	Cu ²⁺
lie de vin	463 nm	Mn ³⁺
bleu altéré	645 et 530 nm	Co ²⁺
violet	597 et 526 nm	Co ²⁺
beige	?	?

Tableau 3 : maxima d'absorption des agents colorants.



Graphique 3 : composition chimique des plages de verre bleu altéré analysées par PIXE.

ABSTRACT

A set of 6 reactive dyes (RD) was suggested, which are covalently bound with $-NH_2$ and $>NH$ groups in any protein bindings (PB), as well as systems of solvents, in which PB are dyed in volume, and the combination of RD with minerals, lipids and polysaccharides is excluded.

An experimental testing of RD and systems of solvents was carried out on models with different distribution, concentration and ageing degree of PB; on different minerals and their mixtures with lipids and polysaccharides; on samples with different combinations of PB with lipids and polysaccharides. The reliability and selectivity of dyeing were compared for RD and acid dyes. It was shown that RD in the investigated systems of solvents can be universal agents for a selective visualization of spatial distribution of PB (films, filling of large cavities, mixtures with minerals) with any painting technique and degree of ageing.

KEYWORDS

Protein binding media; spatial distribution; reactive dyes; painting technique; degree of ageing.

STUDY OF SPATIAL DISTRIBUTION OF PROTEIN BINDINGS IN SITU BY MEANS OF REACTIVE DYES

V.P.Golikov, V.N.Kireyeva
VNIIR
10 Krestyanskaya Pl.
Moscow, USSR

Introduction

Protein bindings (PB) include glutenous glues of collagen materials, casein, the egg white and yolk and protein components of vegetable glues of grain husk. They have been long and commonly used in painting and applied arts. When analysing painting technique and selecting restoration methods, a question often arises of not only the presence of PB, but also of their spatial distribution in a multilayer artistic monument.

One of the principal methods of assessing the distribution is a selective dyeing of PB in microsamples or sections.

For the results of spatial distribution assessment to be objective and reliable, it is necessary to fulfil three basic conditions.

1. Dyes must selectively react with the specific functional groups of PB: $-NH_2(NH_3^+)$ and $NH(NH_3^+)$, absent in minerals, lipids and polysaccharides; the reaction must result in strong chemical bonds between PB and a dye forming an intensive colouring throughout PB volume.

2. A dye must have an opportunity to penetrate the volume of dense PB in the hard phase and reach $-NH_2$ and NH groups. If this condition remains unfulfilled, one may come to a wrong conclusion of the absence of PB in samples with even a large content of PB. In practice, when investigating microsamples this condition is often not met, as the penetration of a dye into PB can be prevented by the following factors:

2.1. A wetting. A poor wetting of PB in the solvent can obstruct the contact of a dye with the PB surface. Fresh PB are hydrophilic and are well wetted by water. However, the presence of lipids in one layer with PB, hydrophobic contamination and also dehydration when ageing diminish hydrophilia and, consequently, the capacity to be wetted by dye water solutions. Solvents are required which wet PB even in such a situation.

2.2. PB density. The density of even fresh PB in the hard phase is fairly high, and $-NH_2$ and NH groups are screened by means of inner- and interchain hydrogen bonds with other PB groups and the hydrate casing. When ageing, owing to interchain lacing and dehydration, the density grows, and $-NH_2$ and NH groups form additional hydrogen bonds, which increases their screening. Dyeing aged PB throughout the volume requires solvents decreasing PB density and, by breaking hydrogen bonds, facilitating the accessibility of $-NH_2$ and NH for dyes.

2.3. Correlation of the surface (S) and volume (V) in PB. Painting monuments may have the following types of PB distribution: films (a) which can be conditionally divided into a_1 - thick (0.5-2 mm) and a_2 - thin (0.01-0.05 mm); fillings of large cracks and cavities (b); a uniform mixture of PB with mineral particles in one layer (c). Since a dye penetrates into the hard phase volume through the surface, the speed and degree of PB dyeing in a sample will depend on the S/V value. In accordance with the growth of S/V the above-said types of distribution can be spaced as: a_1 a_2 b c

It is necessary to ensure the same efficiency of dyeing for all types of PB distribution with different S/V including thick films.

3. Dyes must not be combined with mineral components, and with lipids and polysaccharides either. If this condition is not met, one can come to a conclusion about the presence of PB in samples where PB are absent. In order to reveal PB it is advisable to select dyes which contain no functional groups capable of combining chemically with these components. In a finely dispersed hard phase samples, however, a non-specific sorption is possible owing to the following mechanisms:

- (1) intermolecular interactions due to hydrogen bonds;
- (2) ion exchange due to ion and hydrogen bonds with clay minerals of laminated silicates (groups of montmorillonite, hydro-smuscovite, kaolinite, halloisite), which are basic components of earth pigments and are, as impurities, present in other natural pigments;
- (3) precipitation of insoluble forms of dyes in microcracks and cavities of a finely dispersed sample (microcrystals of a dye and its insoluble salts and complexes with polyvalent cations (Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , Pb^{2+}) extracted from minerals.

In order to fulfil condition 1 this paper suggests, for the analysis of PB spatial distribution, reactive dyes* capable, owing to reactions of nucleophilic substitution or combination, of producing strong covalent bonds with $-\text{NH}_2$ and NH groups in soft conditions: at room temperature, neutral or weakly acid pH.

In order to fulfil conditions 2 and 3 PB were dyed in micro-samples "in situ" not in water, as was suggested to us earlier (1, 2), but in polar organic solvents: dimethylformamide (DMFA), dimethylacetamide (DMAA), dimethylsulphoxide (DMSO) or their mixtures with water. These solvents were selected for the following reasons:

1. Their principal advantage is that they can break fully hydrogen, and partially ion, bonds of $-\text{NH}_2$ and NH groups in PB, and also between dyes and the hard surface of PB, minerals, lipids and polysaccharides. Owing to this, they prevent fully non-specific sorption of dyes through intermolecular interactions and ion exchange, diminish PB density, facilitate the penetration of dyes into the PB volume and render $-\text{NH}_2$ and NH groups accessible for dyeing.
2. They wet well both hydrophilic PB and hydrophobic lipid materials, which facilitates the contact of dyes with the PB surface even after their contamination and ageing.
3. They are weakly volatile, which diminishes the formation of dye microcrystals on the surface of a sample.
4. They solve well both free dyes and their combinations with polyvalent cations, which diminishes their precipitation.

In this work we experimentally tested potentials of reactive dyes and the above - said solvents for assessing the spatial distribution of PB "in situ". Potentials of reactive and acid dyes were also compared, since the latter are at present commonly used for these purposes (3).

Materials and Methods

Selective dyeing methods are very simple. Microsamples or microcross-section are put in a drop of a dye solution**. After having been washed in a pure solvent, the sample is observed under a microscope in reflected or transmitted light***.

We studied 50 dyes with the following reactive groups: mono- and dichlorotriazine (H and M Procions), pyrimidine (Verofixes), vinylsulfonic (Hostalans) amides of carboxylic acids (Lanasols), and for comparison also the most commonly used acid dyes: amido black, green fast, bromophenol blue.

Dyes were tested on single-layer models of minerals and organic bindings**** with three types of distribution: (a), (b), (c) (see ante).

Bindings. PB: glutin of an extract from sturgeon swimming bladder, gelatine, casein, egg white and yolk, whole egg.

* At present these dyes are widely used to dye protein fibres (wool, silk) and in histochemistry (3).

** For determination of dyeing and dye concentration, see post (below).

*** Reactive dyes produce high quality selective dyeing, which makes it possible to make immersion preparations.

**** Homogeneous mixture of minerals and binding in one layer.

Lipids: dammar resin, linseed oil, wax. Polysaccharides: starch, cherry gum and also cellulose.

Minerals. Calcite (chalk, limestone), lime, gypsum, lead white, rutile, zinc oxide, clay materials with high exchange capacity: montmorillonite, hydrous muscovite, kaolinite and halloisite.

We also studied single-layer models "Mineral + Binding" with the mixtures of 2 organic binding ("PB + gum" and "PB + lipids"), as well as double-layer samples with different bindings in each layer.

Dyes were tested in pure DMFA, DMSO and water, as well as in their mixtures with different correlations of solvents in pH ranging from 2 to 9.2.

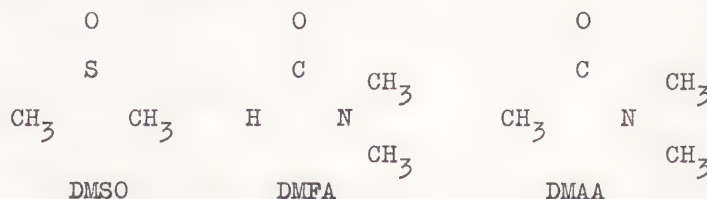
PB in the form of films on glass were aged in two ways: a) by heating at 120°C in air medium for 350 hours; b) by irradiation with SVD-120A UV lamp from a distance of 10 cm. for 350 hours. The degree of dehydration was measured by loss of weight. The intensity of dyeing was assessed visually by the 6-point scale (++++) - very intensive; (+++) - intensive; (++) - moderate; (+) - weak; (+) - not clear; (-) or (O) - absent.

Experimental Results

Selection of dyes. From 50 dyes that had been studied 6 most efficient reactive dyes (RD) were selected of red, blue and green colours*: Procion brilliant blue RC (ICI), (1); Procion brilliant red 5EC (ICI) (II), Cibacron brilliant rot 3BD, 3B-P (Ciba) (III); Lanazol rot 2G (GGG) (IV); Procion green 2BS (ICI) (V); Verofix blau GGL (Bayer) (VI). These dyes have the following reactive groups: dichlorotriazine (I, II, III, V), amide of carboxylic acid (IV) and pyrimidine (VI).

Selection of solvents. As can be seen from Table 2, dyes I-VI in water fall to fulfil all the three conditions: they dye intensively all the PB with type (c) distribution, but dye PB with (a₁) and (a₂) distributions poorly and are not suitable for aged PB films. In addition, these RD in water solutions dye intensively lime and clay materials.

In polar organic solvents RD (I-VI) meet



all the three conditions. The speed of dyeing throughout the volume of even thick films of fresh PB with low S/V is very high (1-3 min). According to speed, the 3 solvents studied can be placed in the following way: DMSO DMFA DMAA

In our opinion, the degree of "driving apart" PB chains, the liquid phase volume between chains and the accessibility of -NH₂ and NH groups in the PB hard phase for RD large molecules in this series of solvents rise, owing to a general increase in the volume of molecules and in the size of hydrophobic fragments.

Water addition changes weakly the speed and intensity of PB dyeing, but increases noticeably solubility of RD and their combinations with polyvalent cations. In so doing, the optimum correlation of an organic solvent and water is 9:1 or 8:2.

Selection of pH. As can be seen from Table 1 RD dye most intensively PB with acid pH, although we know that active groups in I-IV make covalent bonds with -NH₂ and NH in a neutral form, i.e. with pH pK for NH₂ NH₃⁺ in aminoacids - 9-10. This is caused by the fact that the reaction of RD with proteins is two-stage (3).

1) Protonization: -NH₂ -NH₃⁺, NH NH₂⁺ occur at the first

TABLE 2

Interaction of reactive dyes in DMSO - water (pH=5.5) with proteins (PB), lipid (LB), polysaccharides (PS) bindings and minerals

Dye*	Binding type**	pH ^{***}	Dyeing intensity ^{****}									
			LB	PS	Pure minerals					Short alkalies		
			Oil Res. Wax	Starch Gum	Chalk	Lime	White gum	Lead		Short alkalies	Short alkalies	Short alkalies
I	a	++++	++++	++++	++++	++++	++++	++++	++++	+	+	+
II	b	++++	++++	++++	++++	++++	++++	++++	++++	+	+	+
III	a	++++	++++	++++	++++	++++	++++	++++	++++	+	+	+
IV	b	++++	++++	++++	++++	++++	++++	++++	++++	+	+	+
V	a	++++	++++	++++	++++	++++	++++	++++	++++	+	+	+
VI	b	++++	++++	++++	++++	++++	++++	++++	++++	+	+	+

* See the nomenclature of dyes in the text p. 6.

** See the type of binding distribution and evaluation of dyeing intensity in the section "Materials and Methods".

*** See Table 1.

**** Type of distribution see p. 3.

TABLE 1

Estimation of protein bindings (PB) by reactive dyes with different pH in the mixture dimethylformamide / water (9:1)

Dye*	Dyeing intensity of the model "chalk" with uniform PB distribution in onak				
	pH=2	pH=4	pH=5.5	pH=7	pH=9.2
I	++++	++++	+++	++	+
IV	++++	++++	+++	++	+
VI	++++	++++	+++	++	+

Dyeing 30 min.
 x/ The nomenclature of dyes is in the text, p.6
 xx/ Estimation of dyeing intensity see p. 6

* C.I.Reactive dyes: Red 24 (III); Blue 94 (VI); Red 178 (IV). I, II, V - are absent in Colour Index, Third Edition, 1982.

TABLE 3

Comparison of the interaction of reactive and acid dyes with protein bindings (PB), lipids, polysaccharides and minerals

Dyes*	Bindings + chalk with homogeneous distribution (type C)					Minerals		
	PB	Oil	Re-sin	Star-ch	Gum	Chalk	Cyp- Sed	Sheet silicates**
								A B C
H ₂ O, pH = 5.6								
I	+++	-	-	-	-	+++	+++	+++
IV	+++	-	-	-	-	+++	+++	+++
VI	+++	-	-	-	-	+++	+++	+++
VII	+++	-	-	-	+++	+++	+++	+++
VIII	+++	-	-	-	+++	+++	+++	+++
IX	+++	-	-	-	++	+	+++	+++
Dimethylformamide H ₂ O (9:1), pH = 5.6								
I	+++	-	-	-	-	-	-	-
IV	+++	-	-	-	-	-	-	-
VI	+++	-	-	-	-	-	-	-
VII	++	-	-	-	+	+	++	++
VIII	++	-	-	-	+	+	++	++
IX	++	-	-	-	+	+	+	+

*The nomenclature of reactive dyes I, IV, VI is in the text; VII-IX are acid dyes: VII - amido black, VIII - green fast, IX - bromophenol blue.

**Laminated silicates (clay minerals): A - montmorillonite, B - kaolinite, C - hydrous muscovite.

TABLE 4

Influence of ageing on the interaction of reactive red violet 6C with protein binding films

Ageing type X	Solvent	Dyeing intensity				
		Gelatin	Casein	Egg white	Egg yolk	Whole egg
Without ageing (fresh)	A	++	++	++	++	++
	B	+++	+++	+++	+++	+++
Thermic ageing	A	-	-	-	-	-
	B	+++	+++	+++	+++	+++
Photo ageing	A	++	++	++	++	++
	B	+++	+++	+++	+++	+++

Solvents: A - water, pH=5.6; B - dimethylformamide; water (9:1), pH=5.6.

X/Conditions of ageing see p.5-6

TABLE 5

Dyeing with reactive dyes of models "chalk + protein binding (PB)" with different PB content

Dye X	Solvent	Dyeing intensity after 30-minute processing in the mixture of dimethylformamide water (9:1) pH=5.6				
		PB content in %				
		0.5	1	2	4	8
I	A	+	++	++	+++	+++
	B	+	++	++	+++	+++
IV	A	+	++	++	+++	+++
	B	+	++	++	+++	+++
VI	A	+	++	++	+++	+++
	B	+	++	++	+++	+++

X/The nomenclature of dyes is in the text, p.6

TABLE 6

Dyeing with reactive dyes of protein bindings (PB) in combination with gums and lipids*

Serial number	Distribution type	PB types				
		Gelatin	Casein	White	Yolk	Whole egg
1	Model A (mixture white lead + PB)	+++	+++	+++	+++	+++
2	Pure PB film (B)	+++	+++	+++	+++	+++
3	Mixture PB + gum + white lead (C)	+++	+++	+++	+++	+++
4	PB (B) film on mixture M 3 (C)	B	+++	+++	+++	+++
5	Gum (D) film on mixture M 3 (C)	C	+++	+++	+++	+++
6	Mixture white lead + PB ₁ + oil	+++	+++	+++	+++	+++
7	Mixture M 1 (A) layer over oil + white lead (B) layer	A	+++	+++	+++	+++
8	Oil film	-	-	-	-	-

*Dyeing with dye M 111 (see p. 6) in the mixture of dimethylformamide water (9:1), pH = 5.6.

stage with acid pH. Then, by means of SO_2^- or SO_3^- groups*, RD is combined with $-\text{NH}_2^+$ and NH_2^+ as acid dyes. 2) Neutralization $-\text{NH}_2^+$ $-\text{NH}_2$ and NH_2^+ NH takes place owing to the formation of an NH_2^+ ion bond with $-\text{SO}_2^-$ and $-\text{SO}_3^-$. At the second stage a covalent bond is formed between $-\text{NH}_2$ and NH in PB and the RD active group.

The speed and intensity of dyeing PB with pH equal to 2, 4 and 5.6 are comparable Table 2. It is obvious that pH = 5.6 is preferable**.

Concentration of dyes and time of dyeing. The use of concentrated water solutions of RD (0.5-1%) is not desirable because of non-specific sorption on mineral components (see Table 3). In mixtures DMFA: water, where non-specific sorption is suppressed, it is possible to work within a broad range of RD concentrations: 0.01-1%. With 0.1% concentrations the speed of dyeing fresh PB films in these solvents is 5 to 10 min, with 1% concentrations it is 1-2 min.

Hydrolysis of active groups. Hydrolysis of reactive groups takes place in water within 1-2 days, which is accelerated with acid pH values. In non-water solutions hydrolysis is slowed down to several weeks. Therefore, it is advisable to work only with fresh solutions prepared just before dyeing. They can be kept in the form of non-water solutions, and water with pH = 5.6 can be added before dyeing.

The effect of ageing. As can be seen from the results in the table 4, the hard phase aged protein materials are virtually not dyed with water solutions of dyes, and in the mixtures of DMFA + water, with weakly acid pH, the speed of dyeing these films by RD is increased to 20-30 minutes, but then they become fully dyed throughout their volume (Table 4). Light ageing affects little the interaction of PB and RD both in water and in the DMFA + water mixture (Table 4). Thus, RD in DMFA + water mixtures dyes efficiently both fresh and aged bindings. It enabled us to reveal PB films on the surfaces of 11-12th century miniatures on parchment, which could not be found by any other methods.

The effect of PB concentration. As can be seen from Table 5, the intensity of dyeing in the "chalk + PB" samples*** rises as PB content increases both for RD solutions in water and in the DMFA + water mixture. In addition, the intensity of dyeing of pure films (100% PB) in the DMFA + water mixture is considerably higher than that for type (c) samples, where PB is only part of a sample. This enabled RD to be used in the DMFA + water mixture not only for a qualitative, but also for a semi-quantitative assessment of the PB content, for example, for multi-layer ground coats of 12-13th century tempera painting in which layers differ by the content of glutenous glue.

The effect of PB combinations with other bindings. As can be seen from Table 6, for all the investigated PB combinations with lipids and polysaccharides, RD in the DMFA + water mixture dye selectively only layers containing PB. The presence of gums and lipids both in the same layer with PB and in other layers virtually do not obstruct the reaction of RD with PB. At the same time, if PB are present in one layer, and only lipids and gums in the adjoining one, the other layer (without PB) is not dyed by RD. Thus, these experiments make it possible to consider RD in the DMFA + water mixture a universal reagent for the revelation of PB in monuments of art with any technique.

Comparison of reactive and acid dyes. As can be seen from Table 3, acid dyes fail to meet all the above - said 3 conditions (see ante p. 23). They dye PB intensively in water solutions. Many minerals are, however, also intensively dyed in water solutions of these dyes due to non-specific sorption. On the contrary, in the DMFA + water mixture, acid dyes dye minerals poorly, but PB dyeing is negligible, too. The reason is that dyes do not form hydrogen bonds with hard phase in the DMFA + water mixture. Consequently, RD are more reliable in determining PB than acid dyes.

* These groups are present in RD in addition to active groups to increase solubility in water.

** With a substantial quantity of basic carbonates present in the layer, the solution pH must be more acid, as carbonates increase pH.

*** With uniform distribution of PB in chalk (type c).

Conclusion

1. Reactive dyes and systems of solvents are studied, which are able to indicate protein binding media in microsamples of painting.
2. Found reactive dyes interact with protein binding media selectively and do not connect with other binding media (polysaccharides, lipids) and mineral components of painting.
3. Found reactive dyes indicate any types of spatial distribution of protein binding media with any degree of ageing.

References

1. Golikov V.P., Zakharova N.J., Maltseva M.A. Group determination of protein bindings in grounds of tempera painting "in situ" by means reactive dyes. Restoration, investigation, keeping of art monuments. Information center of problem of culture and art. M., N 1, 1981.
2. Golikov et al. Opportunities of application of reactive dyes for group identification of protein binding in grounds of tempera painting. Art Heritage (Keeping, investigation, restoration). V.9(39), 1984, p. 76-87. M.
3. Ivanov V.B. Reactive dyes in biology. Publication "Nauka", M., 1982.

ABSTRACT

ANALYSIS OF SPATIAL DISTRIBUTION OF HYDROPHOBIC RESTORATION MATERIALS BY MEANS OF FLUORESCENT PROBES

Fluorescent probes (FP) were suggested to analyse spatial distribution of hydrophobic natural and synthetic restoration materials (HRM) in monuments with a prevailing mineral phase. Experimental proof is given that fluorescent probes, that were found, luminesce selectively only within HRM and do not luminesce in chemical bonding and non-specific sorption with a mineral phase. FP make it possible to visualize any types of HRM distribution (films, filling of large cavities and cracks, uniform impregnation) in the two-phase systems of "HRM + mineral". Characteristics are given of spatial distribution of solutions and dispersions of some synthetic polymers in model chalk samples, obtained by means of FP.

V.P.Golikov, Z.F.Zharikova
10 Krestyanskaya Pl., VNIIR
Moscow, 109172
U.S.S.R.

Introduction

The principal stage of restoration is impregnation of the surface or full volume of a monument with consolidating materials in the form of solutions or dispersions. Obviously, an objective estimate of their spatial distribution is necessary for the right choice of materials and techniques of their injection into the monument. Methods of such estimate (1-3) applied at the present time, are not widespread in technological investigations and restoration practice.

In this paper we investigate possibilities of fluorescent probes (FP), organic compounds, possessing intensive visible luminescence in restoration materials, for a simple and vivid visualization of these materials. At the first stage we found several FP* suitable for visualization of hydrophobic restoration materials (HRM) in monuments where mineral phase prevails (stone, mortar, plaster, ground and paint layers of wall painting with a mineral binding or degraded organic binding material**).

Materials and Methods

The technique of estimating spatial distribution of HRM in two-phase samples "HRM + mineral" is quite simple. FP solution*** is applied to the surface or cross section of a two-phase sample, and after the solvent has dried, is illuminated with any UV source of light****. Acridine and porphyrine FP, found in the course of this investigation, luminesce selectively only within the volume of HRM, therefore, one can clearly and vividly see HRM and their distribution on the surface by intensive luminescence against the background of dark mineral phase.

FP have by now been tested for the following materials:

Minerals. 1. Calcite (chalk, limestone). 2. Lime. 3. Gypsum. 4. White lead. 5. Rutile. 6. Zinc oxide. 7. Yellow ochre (hematite + kaolinite). 8. Red ochre (hematite + kaolinite). HRM Natural: Resins (dammar, mastic, copal, shellac, gum lac, elemi, rosin, frankincense, Venetian turpentine). Oils (linseed sunflower, olive), beeswax, lecithin. Synthetic polymers: water dispersion of vinylacetate copolymer with ethylene (85:15 relatively) - CBЭД-33 (SVED-33) and CBЭД-50 (SVED-50), where 33 and 50 are concentrations of the polymer dispersions (the size of CBЭД-50 (SVED-50)), dispersion particles is 1.5-2 times as much as those of CBЭД-33 (SVED-33); partially hydrolysed vinylacetate copolymer with ethylene, CЭВ (SEV) (2:1 solution in alcohol-water mixture); BA-2ЭГА (VA-2 ЭГА) - water dispersion of vinylacetate copolymer with 2-ethylhexylacrylate. PBMA - poly-n-butylmetacrylate. BMC-5 - butylmetacrylate copolymer with 5% metacrylic acid. PVA - polyvinylacetate (dispersion). K-15/3 - siloxane resin.

Experimental Check of Fluorescent Probes Suitability

In order to isolate reliably and objectively HRM in two-phase samples "HRM + mineral" FP must fulfil two principal conditions:

1. To luminesce selectively only within the HRM volume at any HRM distribution.
 2. Not to luminesce when interacting with minerals and at non-specific sorption on the surface of both minerals and HRM.
- Experimental proof that FP, that have been found, fulfil these conditions is given below.

*At present, FP are being patented, that is why their formulas are not given here.

**At the next stage we propose finding FP for other restoration materials and for HRM in painting with organic binding materials.

***See post about the selection of solvents.

****A portable UV chromatographic lamp was used in this investigation for a visual estimate of HRM distribution.

KEYWORDS

Restoration materials, fluorescent probes, synthetic polymers, impregnation depth.

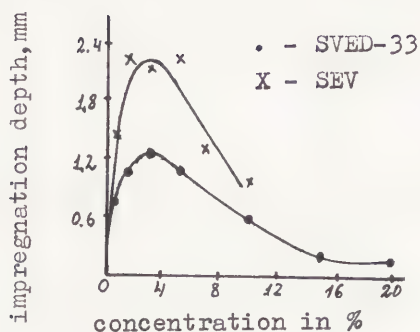
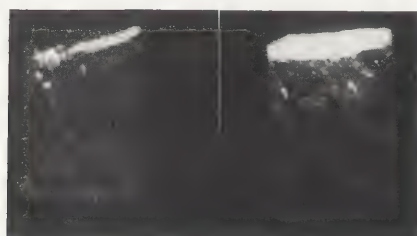


Fig. 1. Dependence of the impregnation depth of the chalk block on the SVED-33 and SEV concentration.



A

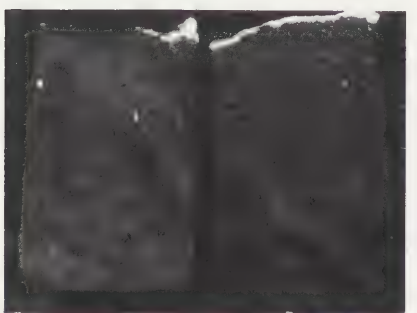
B



C

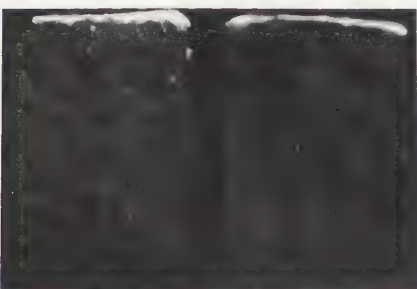
D

SVED - 33
enlargement - x3



a

b



c

d

SVED - 50
enlargement - x5

Interaction of Fluorescent Probes with Hydrophobic Restoration Materials

1. Two-phase "HRM + mineral" models with well-known types of HRM distribution in the mineral phase have been prepared:
 - a) film on the surface; b) filling of large pores and cracks; c) uniform impregnation of the mineral phase volume. FP reveal clearly each of these types of distribution.
2. If FP is introduced into HRM solution or dispersion, applied to glass and dried, the resulting HRM film luminesces intensively.
3. If a fixed quantity of a mineral is mixed with a solution or dispersion of HRM of different concentrations and then dried, after treatment with FP, luminescence intensity increases with a rise in HRM concentration in a two-phase sample.
4. A two-phase "HRM + chalk" sample was prepared as described above. Chalk was then dissolved in HCl, and the excess of HCl and CaCl_2 was removed by treatment with H_2O up to pH=7. Luminescence intensity, before and after chalk has been dissolved, was practically the same.
5. HRM solution was applied to the surface of a mineral block. Intensely luminescent HRM spot could be clearly seen after treatment with FP. Repeated treatment with H_2O , which dissolves FP well, but does not dissolve HRM, did not change luminescence intensity or the HRM spot. After that, the spot was treated once with ethanol dissolving well both FP and HRM. Intensity of the spot went down sharply, since ethanol dissolved HRM with FP, and the solution penetrated into the depth of the mineral block, so that the HRM content on the surface decreased drastically. Consequently, FP are linked not to the surface, but right with the HRM volume.
6. An HRM spot, the same as in paragraph 5, was treated with 12 different FP, having the same heterocyclic skeleton, but with different substituents. Intensity of all 12 FP in the solution was comparable, so that intensity of HRM luminescence after treatment must be linked only to the degree of combining FP and HRM. Luminescence intensity of each HRM after treatment with FP depended very much on the nature and number of substituents in these FP.
7. For each FP one can select solvents in which its luminescence is weaker than in the HRM volume. Having placed a piece of HRM in FP solution, one can watch in a luminescent microscope how FP from the solution penetrates gradually into the volume of this piece.

Interaction of Fluorescent Probes with Minerals

FP in solutions can be chemically combined with functional groups of minerals. In addition, non-specific sorption always occurs on a finely dispersed surface of the mineral phase at the expansion of intermolecular interactions (mostly hydrogen bonds), local precipitation in cracks and recesses of microcrystals and formation of non-soluble FP combinations with polyvalent cations. Luminescence for all the above-described types of interaction with minerals was investigated. Mineral powders and blocks were placed in diluted FP solutions in organic solvents, possessing, in addition to luminescence, also colouring*. In 20-30 minutes mineral particles were coloured, partially owing to chemical combination, and partially as a result of sorption owing to intermolecular interactions of FP. Coloured minerals were treated with dimethyl formamide (DMF), which removes FP not chemically combined with the mineral. Intensity of colouring diminished but was partially preserved. Minerals, coloured by FP, luminesce neither before, nor after treatment with DMF. Consequently, FP, both chemically combined with and adsorbed on minerals, produce non-luminescent forms. Monocrystals of FP and insoluble compounds of FP with cations Ca, Fe, Mg, Al, Pb, Zn were precipitated on the surface of mineral powders and blocks. There was no luminescence of FP in both cases.

The above experiments show that FP can be combined both with HRM and with minerals like ordinary dyes; in so doing HRM and minerals in two-phase samples cannot be distinguished. FP luminesce, however, only within the HRM volume, and FP do not luminesce in all types of combinations with minerals. Consequently, FP selected fulfil the two above-said conditions and can be used for a selective revelation of HRM and visualization of their spatial distribution in the two-phase samples "HRM + mineral".

*Diluted solutions in organic solvents were used to reduce as much as possible precipitation of microcrystals and insoluble combinations with polyvalent cations.

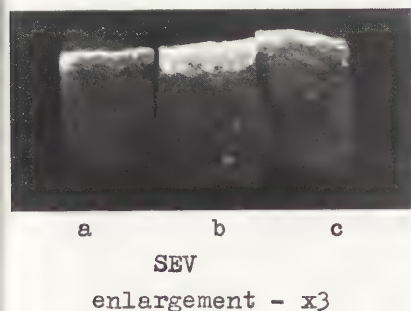


Fig.2 Dependence of the impregnation depth on the concentration of the solution or dispersion; for SVED-33 and SVED-50: a-0.5%, b-3%, c-10%, d-20%; for SEV: a-0.5%, b-3%, c-10%.

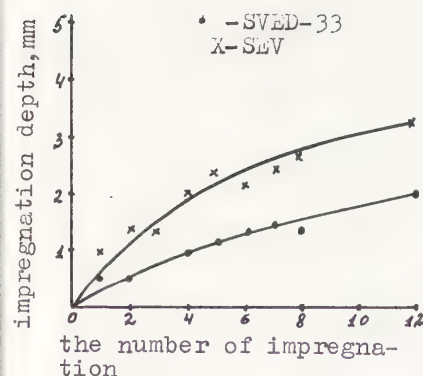
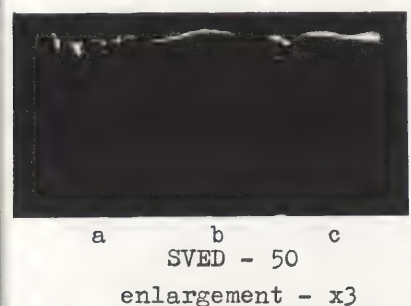
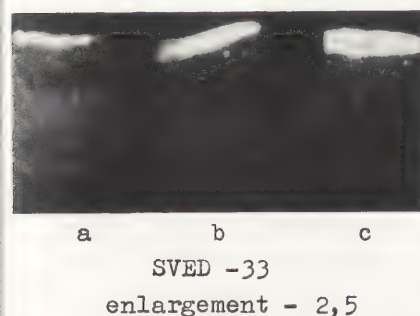


Fig.3 Dependence of the impregnation depth of the chalk block on the number of impregnation for SVED-33 and SEV



Owing to such selective luminescence, the FP method is considerably more efficient and reliable than the technique of selective colouring of HRM with special dyes, since in a finely dispersed sample with an excess mineral phase it is difficult to distinguish dyes, combined within the HRM volume and non-specifically absorbed on the surface of minerals.

Fluorescent Probes Technique Limitations

In the course of practical application of FP to estimate spatial distribution of HRM in the two-phase samples "HRM + mineral" the following problems may arise:

1. In the mineral phase there are often present soluble combinations of paramagnetic Fe and Cu cations capable of reducing drastically FP luminescence. In order to avoid this effect it is necessary either to use solvents in which Fe and Cu combinations are insoluble, or to add complexons to FP solutions, which obstruct the interaction of Fe and Cu with FP.

2. FP luminescence depends on pH of their solution. Therefore, for each FP it is necessary to select optimum pH and take into account the fact that some minerals can change pH of FP solutions.

3. For HRM to be visualized in the two-phase samples FP must penetrate from the solution into the HRM volume. The extent of this penetration depends on the structural correspondence of FP and HRM and on the size and density of the HRM phase. For this reason, FP, which penetrate well into HRM particles 1-5 μ m in diameter, it being impregnated uniformly, penetrate poorly into 5000-10000 μ m - thick films, and they do it better into freshly impregnated samples than into aged ones, with tightened HRM.

Therefore for a better visualization of each HRM it is necessary to select most efficient FP, as well as such systems of solvents, in which FP would penetrate into HRM at any type of its distribution and the extent of tightening.

4. Chromatographic separation of HRM and FP occurs if FP is into HRM solution or suspension, and then the mineral block is impregnated. This is accounted for by the fact that HRM and FP are not chemically combined. The degree of separation is determined by ordinary factors of column chromatography: the nature of FP and HRM, as well as by the composition and structure of the mineral phase.

In order to exclude the separation effect FP were introduced into the two-phase samples after the distribution of HRM in the mineral phase.

It is possible to introduce FP directly into HRM solution or dispersion only in cases when the mineral phase contains many Fe and Cu combinations. Then luminescence of FP, which did not get into the HRM volume, would be dampened, and FP luminescence in the HRM volume, though diminished, would still produce a distinctive luminescent contrast.

Fluorescent Probes Application

Certain regularities of spatial distribution of synthetic polymers on mineral substrate have been studied by means of FP C β B (SEV) solutions, as well as CB β D-33 (SVED-33) and CB β D-50 (SVED-50) water dispersions, were introduced into model chalk samples.

Samples were prepared in the following way: chalk was mixed with water till it was as thick as sour cream, then placed in a mould and dried with the resulting 2x2x0.5 cm samples. Such a sample was cut across into two halves, and polymer solution or dispersion was applied by means of a pipette on the cross section. Each impregnation consisted of one drop. When investigating the dependence of impregnation depth on polymer concentration and solution nature the number of impregnations was 6, i.e. 6 drops, as with this amount, first, film was not yet formed on the surface, and, secondly, adsorption went on sufficiently fast. A cross section was made after impregnation, so that two symmetrical samples were obtained; they were treated with FP solution in specially selected solvents and studied in a stereomicroscope with a 20-100 diopter scale and with a chromatographic lamp as a UV source. It is possible to measure quantitatively the distribution of polymer in a chalk block by means of a microfluorimeter.

Dependence of impregnation depth on concentration of restoration polymer materials. As can be seen from Fig. 1 and 2, this dependence is extreme for CB β D-33 (SVED-33) and C β B (SEV). When concentration varies from 0.5 to 3% impregnation depth rises, with a further increase up to 20% it falls. The maximum impregnation depth for CB β D-33 (SVED-33) and C β B (SEV) is observed with a 3% concentration and constitutes 1.3 mm for CB β D-33 (SVED-33), and 2.3 mm for C β B (SEV). Lesser impregnation depth at lower concentrations seems to be linked to the fact that the

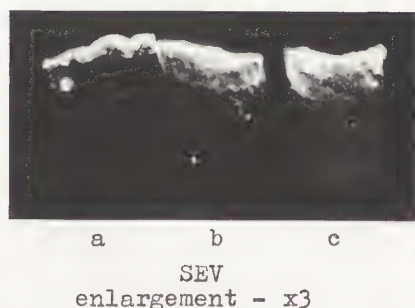


Fig.4 Dependence of the penetration depth of the restoration material into the chalk block on the number of impregnations: a-1 drop, b- 4 drops, c- 8 drops.

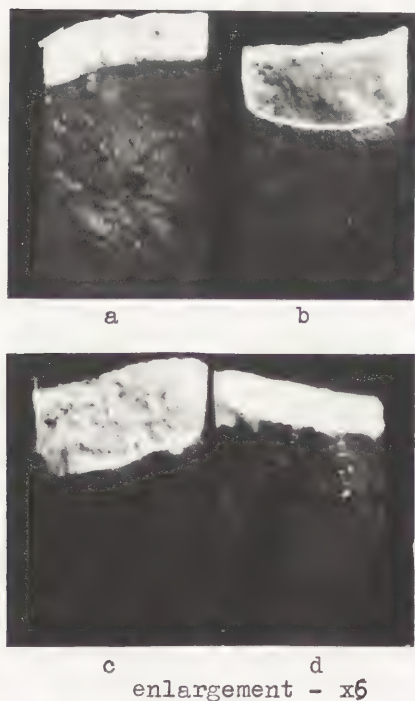


Fig.5 Dependence of the impregnation depth with 3% concentration SVED-33 on the solvent: a-toluene, b-acetone, c-dimethylacetamide, d- water.

given quantity of polymer material is not sufficient to fill up a greater volume of the chalk block. Impregnation depth at lower concentrations can evidently be increased by increasing the number of impregnations. The dependence of polymer penetration depth on the number of impregnations at a given concentration will be considered later on.

A decrease in impregnation depth at higher concentrations is caused by the fact that polymer film is formed on the surface of the chalk block, which prevents additional polymer portions from penetrating into the depth of the block. CBЭД-50 (SVED-50) does not virtually penetrate into the chalk block, as can be seen from Fig. 2, it forms film on the surface at all concentrations.

Dependence of penetration depth of polymer materials with the number of impregnations. The given dependence is shown in Fig. 3 and 4. The results were obtained for 3% concentration CBЭД-33 (SVED-33), CBЭД-50 (SVED-50) and CЭВ (SEV). As the number of impregnations increases, penetration depth of polymer materials into the chalk block is growing, more drastically at first impregnations, at further ones, penetration depth diminishes. CЭВ (SEV) has greater penetrating capacity: with 8 impregnations penetration depth constitutes 2.7 mm, for CBЭД-33 (SVED-33) it is 1.5 mm. CBЭД-50 (SVED-50) (Fig. 4) produced film on the surface of the block at first impregnations. The maximum penetration depth of CBЭД-33 (SVED-33) is 2.4 mm, which is achieved with 17 drops, when film is formed on the chalk surface, so that a further increase in the number of impregnations is of no use: new portions of polymer would only cause thickening of the film and would not get inside the block. 17 drops of CЭВ (SEV) solution penetrate to a 4.5 mm depth. As thick film as with CBЭД (SVED) is not formed, but the surface shines, which indicates an increase in the concentration in the surface layer.

Dependence of impregnation depth on the nature of the solvent. This dependence was studied for 3% concentration CBЭД-33 (SVED-33) solutions. Toluene, acetone and dimethylacetamide (DMAA) were used as solvents. Impregnation depth in these solvents was compared to impregnation depth of CBЭД (SVED) water dispersion of the same concentration (Fig. 5). In all cases 6 drops of solution or dispersion were applied to the chalk block. In accordance with the increase in impregnation depth the solvents were grouped in the following order: water toluene acetone DMAA. It should be noted that CBЭД (SVED), in the form of water dispersion, forms the most compact and uniform layer in the chalk block, and, in the case of DMAA solvent, polymer concentrates more on the edges of the impregnated chalk layer, i.e. moves prevalently with the front of the solvent.

Conclusion

1. A selection of fluorescent probes, which fluoresce only in polymers and do not fluoresce in minerals, was made on the basis of a research into the interaction of fluorescent probes with polymers and minerals.
2. Certain regularities, occurring when chalk blocks are being impregnated with CBЭД (SVED) dispersion and a CЭВ (SEV) solution, were detected by means of the probes selected

Bibliography

1. Heidingsfeld V., Smejkalova Z. Zpevnování omítky disperzemi a roztoky polymeru. II. Merení hloubky penetrace. Sborník Vysoké školy chemicko-technologické v Praze. 1983, S. 10, S. 215-222.
2. Hrdlická Z. Analýza penetrace ochranných nater do stavebních materiálů. Výzkumná zpráva UIV REZ, 1979.
3. Hrdlická Z. Neutronografická analýza některých speciálních problémů aplikace penetrátoru na stavební hmoty. Výzkumná zpráva UIV REZ, 1980.

ABSTRACT

The present work is devoted to studying chemical compositions of the fillers and binders used in over 200 oil paintings by the Russian and foreign painters worked in Russia in the 18th century. In the course of the study use was made of the microchemical, emissive spectrum and microscope analyses.

KEYWORDS

Analysis, binder, composition, conservation, filler, ground, painting, treatment.

THE MATERIALS FOR PAINTING USED BY THE RUSSIAN AND FOREIGN PAINTERS WORKED IN RUSSIA IN THE 18TH CENTURY

Galina N. Gorokhova and Marianna G. Kononovitch
Grabar Conservation Centre. 60/2, B.Ordynka,
Moscow USSR.

The present work is devoted to studying chemical composition of the fillers and binders used in over 200 oil paintings by the Russian and foreign painters worked in Russia in the 18th century.

It is common knowledge that the grounds play an important part in art-works' creation. They influence not only the texture and colouring of paintings, but also the state of their preservation, meet the adhesion of paint layers and supports, absorb excess of binders from paint layers, prevent from binders' penetration from paint layers into supports.

The knowledge of the particular features give the conservator a tool which he uses both in choosing the method of conservation treatment and in diagnosing the cause of damages on a painting; while to the art critic - the material for studying the paintings' techniques expert appraisal and attribution of the given piece of art.

In the course of the grounds' study use was made of the microchemical, emissive spectrum and microscopic analyses. We used the microscopic analysis for identifying the chemical composition of the materials involved. The same was used for identifying the fillings-in and the coats in the grounds. The ground microsections which we specially prepared for the purpose were studied in the reflected light with the aid of horizontal metallographic microscope.

All the samples analysed were washed off the binders as the latter have darkened with the time passed and together with the conservation remedies changed the original colour and the texture of the ground. A lot of the grounds which at first looked like single-primed turned out multi-primed.

Thus, we can come to the following conclusion.

It was single-primed glue grounds that were used by the Russian artists in the first quarter of the 18th century, and they were brown, red-brown, and also yellow-brown in colour, with a latter being an exception. The foreign artists worked in Russia in this period used all the three types of the grounds without exception. The main components of the grounds' fillers were ochers (brown, red-brown, or yellow-brown), umber, sienna, bolus.

Apart from the single-primed grounds, double-primed ones also came into use at the beginning of the 50s. The upper coat was yellow or light yellow (yellow ocher mixed with chalk or with lead white as the fillers), while the lower coat was darker one (red-brown, brown and dark brown ochers as the fillers). In that period of time, the emulsion grounds were in use. The binder in the upper coat contained oil and glue. There appeared the paintings on single-primed light coloured grounds (yellow ocher or yellow ocher mixed with chalk as the fillers).

Thus, darker grounds gave place to lighter ones. As for the foreign artists, we can meet the grounds of such a type, with light upper coats (yellow, pink) and darker lower ones, at the beginning of the 1730s. Yellow coloured single-primed grounds came into their use in the 50s. The fillers and binders were identical ones.

In the second half of the 18th century, and, more precisely, at the end of the 50s - the beginning of the 60s, the Russian painters used the double-primed grounds in which the upper coat was grey in colour. In that case, for the upper coat as the fillers they used lead white mixed with a black pigment of organic origin (burnt bone, soot, charcoal black), or a black mineral pigment, sometimes mixed with chalk, red or brown ocher, while in the lower coat - ochers of various tints, or the same ochers mixed with lead white. The binders in the upper coat contained oil and glue. Glue predominates in the lower coat, sometimes it appears mixed with oil.

The foreign painters started working with the grounds of this type in the 1740s. The fillers and binders of the grounds are the same. Side by side with these double-primed grounds they made use of the dark single-primed ones up to the end of the 18th century.

At the end of the 18th century, there appeared double-primed grounds with the white upper coat (oil as the binder and lead white or lead white mixed with chalk as the fillers) and the coloured lower coat (glue as the binder and ochers of different colours, umber, sienna as the fillers).

At the end of the 18th - the beginning of the 19th centuries, the Russian painters started working with the white single - primed grounds with lead white mixed with chalk as the fillers. The grounds with pure chalk as the filler we can meet amongst the paintings of Ukrainian School. Thus, the study of the grounds in the paintings by the Russian and foreign artists worked in Russia all throughout the 18th century demonstrates that there were no considerable differences in the materials - the main components and the admixtures used. Oil and glue were used as the binders; chalk, lead white, ochers (brown, yellow, red), umber, sienna, bolus, black pigments of organic origin (burnt bone, soot, charcoal black), or a black mineral pigment, vermilion, auripigment - as the fillers.

Thus, as the result of the study we have brought out the basic tendencies of the grounds' construction and their evolution in due course.

LITERATURE

Gorokhova G.N. and Kononovitch M.G. Study of the grounds used by the Russian painters in the 18th century. Moscow, 1986.

Gorokhova G.N. and Kononovitch M.G. Study of the grounds used by the foreign artists worked in Russia in the 18th century. Moscow, 1988.

ABSTRACT

In measuring by X-ray diffractometry, the position sensitive proportional counter(PSPC) covers 150 degrees of X-ray diffraction, continuously. The data are accumulated by the multichannel analyzer(MCA) and monitored on CRT during measurement period. Mounted sample can rotate around three axes. Then the XRD spectra are very like to those from wide angle goniometer(powder). This system measures an area from 10 to 100 microns in diameter. So, not only small samples, but also small portions in the matrix are measured by this system. Feasibility of this system for art and archaeology will be discussed.

KEYWORDS

Pigment, Mineral, Pearl, Micro diffractometry, XRD, Analysis

MICRO X-RAY DIFFRACTOMETER(PSPC/MDG) SYSTEM FOR THE STUDY OF WORKS OF ART

Masamitsu Inaba*, Jun-ichi Miyata, Ryuitiro Sugisita
Conservation Laboratory
Tokyo National University of Fine Arts and Music
Ueno Park, Taito-ku, Tokyo, 110, Japan

INTRODUCTION

X-ray diffractometry is one useful method for determining the crystalline compounds. However, amounts of samples for X-ray diffraction(XRD) taken from artistic or archaeological objects are usually limited. Then it is often unsuccessful to get XRD spectra from powder samples using a wide angle goniometer. For getting XRD spectra from microamounts of samples, many researchers have been using an XRD camera. It is rather time consuming work to get even an XRD spectrum. To compare a normal powder XRD pattern, converting the spectrum on film into digitized values using densitometer is needed. Lahanier classified the XRD equipment to the size of the samples to be analyzed(1). In his paper, a Gandolfi camera and a microdiffractometer equipped with a circular detector are classified for the smallest samples. In this paper, we describe a feasibility of a new micro XRD spectrometer, manufactured by Rigaku, installed in our laboratory in 1988.

Instrument

Rigaku RAD-RC (12 kW)
Rotating tube: Cu, Filament:10 x 1 mm(point configuration)
K-beta filter: Ni
Collimator(diameter): 100, 50, 30 and 10 micrometer
PSPC/MDG(position sensitive proportional counter/
micro diffractometer)
Multichannel analyzer(MCA)
Personal computer(Casio, 16 bit CPU: V30)

Curved position sensitive proportional counter(PSPC) can cover 150 degrees of X-ray diffraction, continuously. PSPC can reduce measuring time to a great extent, comparing with scanning type counters. These data are accumulated by a multichannel analyzer(MCA) and monitored on CRT during the measurement period. It means that we can know the favorability of a setting of each sample in a short time, and decide easily the appropriate length of measuring period. If a feature of a spectrum was bad, we could try to change the setting of the sample. This is a great advance of micro diffractometry, since at other systems, such as camera method, we reveal such a mistake in setting of a sample after finishing of a time consuming measurement.

Measuring of smaller samples, heterogeneity in Debye-Scherrer ring is increased by reducing amounts of powder particles participating to X-ray diffraction. To solve this problem, the sample should be rotated around two or three axes; chi(360°), phi(±30°, ±40°) and/or omega(40°)(See fig. 1). Gandolfi camera also rotates the sample around two axes. On the other hand, Rigaku's old micro XRD apparatus does not need to rotate the sample, since it has a circular detector to detect a whole diffraction cone in a Debye-Scherrer pattern. However, this detector should scan the XRD spectrum of the sample. Rigaku already quitted the production of this type of apparatus.

Maximum size of a sample is 6 mm x 6 mm x 6 mm. We currently measure small particles and cross-sections of paint layers, so we did not modify the micro XRD system for the study of works of art.

MEASUREMENT OF ART OBJECTS

A sample is set under a microscope(x160) using cross wire(x,y) and focus(z). Focusing the sample is often difficult, especially in the case of rough surface, and we may often miss the setting of the sample. So, a sample should be mounted on a small plastic rod with double coated Scotch tape. In this technique, we can rotate the sample on the rod to get flatter surface against the X-ray beam.

A small fragment of a pearl in a necklace in Roman period(2), was analyzed. The XRD spectrum is shown in Fig. 2. From this spectrum, the sample was identified as aragonite(Calcium

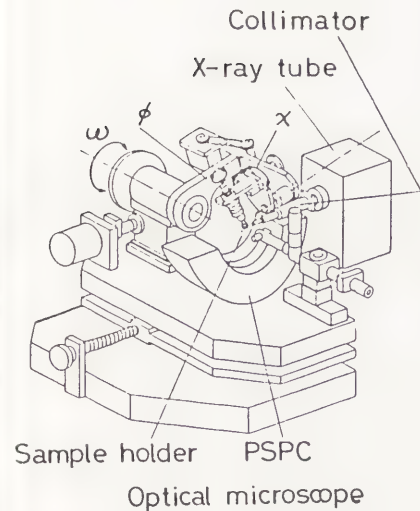


Fig. 1
Diagram of PSPC/MDG.

carbonate).

In Japan, sampling from a cultural property is often limited. Then, some researchers use the Rigaku's non-destructive XRD system(3). However, identification of small particles dispersing in large amounts of other materials is difficult by the non-destructive XRD system, since XRD spectrum of the sample is hidden by the strong XRD spectrum of the matrix. The XRD spectrum of the sample taking out from the matrix shows many lines of XRD, and bring more accurate identification than the XRD spectrum using non-destructive XRD system does(3,4).

For a large sample, such as a cross-section of a painting layer, we cannot measure the 2θ less than 20 degrees. This reduces the number of low angle lines in the pattern(See figs. 3,4).

In our experiences for small particles in matrices or thin layered samples, e.g. wall paintings of Dunhuang Cave in China(5), around 20 microns in diameter of a particle or in thickness of the each layer might be the smallest limit to get practical signals using 30 microns of collimator. There are two reasons. First, using a filament of normal size(1x10 mm), with point configuration, at 12 kW(60 kV, 200 mA), even the signals of Si at the 10 microns of collimator are very weak. Since the intensity of X-ray diffraction varies in proportion to the area of X-ray beam. Secondly, to set a sample at the right position of the center of rotation of 3 axes within a deviation less than a few microns is difficult. It has a tendency to move from the center position mechanically by the temperature change in the chamber of MDG system.

Accumulation time is 1000-2000 sec(40 kV, 150 mA, 100 microns of collimator) for a normal sample and is 3000-10000 sec(55 kV, 200 mA, 30 microns of collimator) for a small sample(around 20 microns).

DATA HANDLING AND IDENTIFICATION

Accumulated data in MCA are put into a personal computer. Channel number for each datum from PSPC should be converted into 2θ value compare known signals of a standard material. Powder Si is usually used as a standard material. Lowest 2θ value of Si is 28 degrees(Cu K-alpha), so the values below it should be extrapolated. We had encountered a great deviation from correct angles at lower angle region. It may be caused from a deformation of the wire in the PSPC. Then we use other standard materials, mica or talc, when we need to calibrate lower lines of XRD.

After processing the spectra, e.g. smoothing for shapes, background subtraction and peak identification, d-values and intensities of peaks are calculated automatically and/or manually by the personal computer. The search match software in our system is not sophisticated too much. In the view of the pattern of XRD signals against JCPDS(Joint committee of powder diffraction standards) signals on the CRT, this software is very helpful for operators.

CONCLUSION

We feel the PSPC/MDG system is useful for analysis of very small particles and these in matrices.

REFERENCE

- 1) C.Lahanier, "The Powder Diffraction Pattern Applied to the Knowledge of Works of Art", Chemica Scripta, 26A(1986): 47-55.
- 2) Y.Matsuda and S.Matsuzuki, "Analysis of a Pearl Used in a Necklace in Roman Period" (Paper derived at the Tenth Annual Meeting of Kobunkazai Kagaku Kenkyû-kai, Tokyo, May, 1988), 20.
- 3) M.Koyano and T.Kadokura, "A Preliminary Report on the Examination of Crystals Found on Oil Paintings in Japan Using Non-destructive X-ray Diffraction", (Paper derived at the Eighth Triennial Meeting of the International Council of Museums Committee for Conservation, Sydney, September, 1987), 59.
- 4) J.Miyata, "Analysis of the Crystalline-like Substances Observed on the Surface of Oil Paintings", Kobunkazai no Kagaku, 32 (1987): 21-30.

- 5) S.Duang, J.Miyata, N.Kumagai and R.Sugisita, "Analysis of Pigments & Plasters from the Wall Painting of Buddhist Temples in North Western China", *Kobunkazai no Kagaku*, 32 (1987): 13-20.

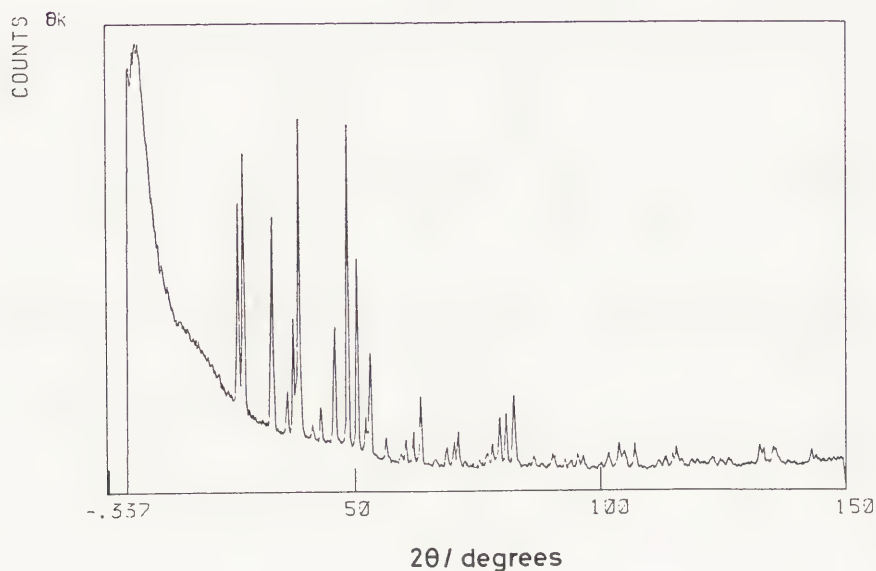


Fig. 2 XRD spectrum of a fragment of a pearl in a necklace in Roman period.

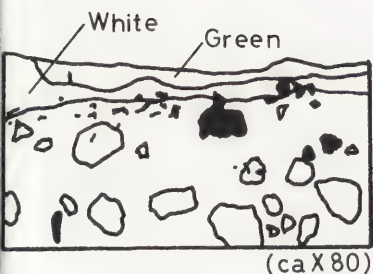


Fig. 3 Diagram of a cross-section of a fragment picked from a wall painting from Dunhuang Cave No. 55, 10-11 Century.

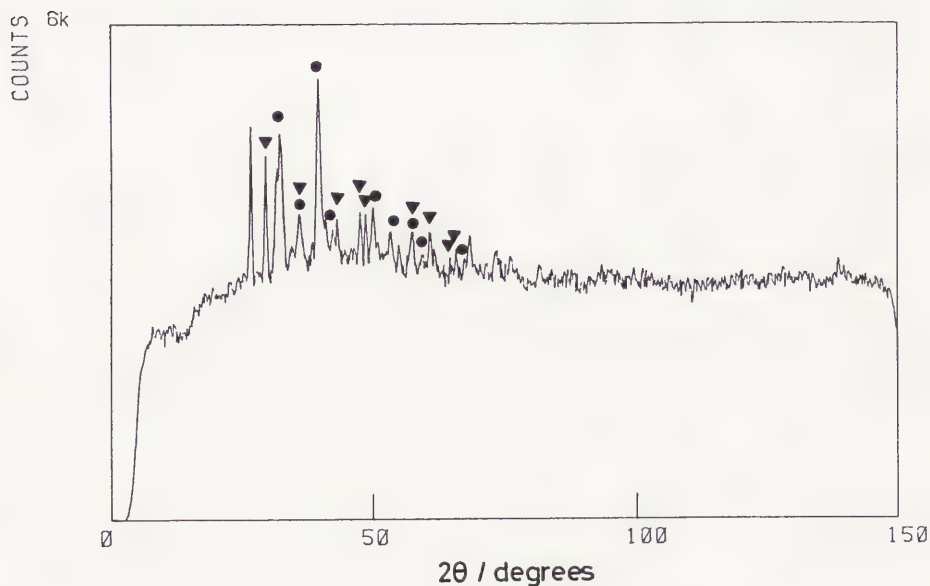


Fig. 4 XRD spectrum of the green layer of the cross section (Fig. 3).
(● Atacamite, ▼ Calcite)

SUMMARY

Dendrochronology as an analytical tool for dating of wooden art-objects has been used for the last 20 years and had basically been restricted to oak wood in general. Several years ago, dendrochronological analysis was initiated for the wood of different conifer species used in art-objects. For spruce and pine wood new chronologies were established for different regions, for fir wood an existing master chronology from Southern Germany could be used. These chronologies now allow an exact time-related determination of the last growth ring available on an object. From this result several conclusions can be derived with respect to the felling date of the tree and also for a "terminus post quem" of the art-object. Although in principle, dendrochronological analysis is always possible, its application is often limited if boards have been tangentially sawn or if the boards are small and do not contain a sufficient number of rings.

KEYWORDS

dendrochronology, panel paintings, spruce wood, fir wood, pine wood.



Fig. 1 a:
H. Holbein the Elder:
"Flagellation" (photograph:
Fürstenbergssammlungen Donaueschingen)

TREE-RING CHRONOLOGIES OF CONIFER WOOD AND ITS APPLICATION TO THE DATING OF PANELS

Peter Klein,
University of Hamburg, Chair of Wood Biology
Leuschnerstrasse 91, 2050 Hamburg 80
Fed. Rep. Germany

Introduction

Several years ago, a comprehensive investigation of the wood of different kinds of conifer species, e.g. Norway spruce (*Picea abies*), Silver fir (*Abies alba*), Scots pine (*Pinus sylvestris*) and Stone-pine (*Pinus cembra*) had been initiated by the University of Hamburg and the Gemäldegalerie Berlin-Dahlem with financial support by the Volkswagen Foundation.

In a first step, different panels of conifer wood were analysed for species determination. Catalogues and other descriptions in the museums indicating the kind of wood involved were generally unusable because species identifications were botanically incorrect leading to much confusion. The primary aim was then to establish chronologies for different species or to use available chronologies for dating the wood of panels.

Material and Methods

In order to establish a chronology for spruce and pine wood statistical measurements of chronological compatibility of recent trees within and between different regions were carried out in particular for the forests in the northern and southern parts of the Federal Republic of Germany.

In addition, 150 panels of different conifer wood and 250 string instruments were investigated at different museums in Europe and the United States of America (Klein 1985, Klein, Bock 1989).

For spruce wood, three chronologies were established and three other, existing chronologies used. For pine wood, a new chronology was established for the northern part of West-Germany. For fir wood, the establishment of a new chronology was unnecessary because the chronology of Becker and Giertz-Siebenlist (1970) allows the dating of panels. For stone-pine, a chronology could not be established because the single boards did not contain enough rings. However, it may be possible to apply the chronology of Siebenlist-Kerner (1985) also for dating of stone-pine panels.

Application of the chronologies for dating of panels

Spruce Wood

The chronologies of spruce wood established for dating of string instruments can also be used also for dating panels. A chronology for the alpine region, for example, has been successfully used to date several panels of the cycle "Graue Passion" (Fürstenbergssammlungen Donaueschingen) created by H. Holbein the Elder (Table 1; Fig. 1a, b).

The two panels consisted of seven boards of spruce wood and it could be shown by the growth ring structure of each board that they represented the back- and the frontsides in earlier time. The youngest ring on the panel had grown in the year 1482. Under the assumption that with spruce wood only the bark had been removed and the entire tree used, a felling date of 1482 can be derived. With an assumed storage time of 10 years, as probably customary in the 15th century, creation of the two panels would be plausible from 1492 onwards.

An other example can be given for four pieces of an altar of the circle of W. Pacher (1435-1498) (National Gallery, Washington). Two of the panels were composed of 4 boards and two by three boards. The youngest growth ring had grown in the year 1495. That means, under consideration of the storage time that the panels were made after the death of W. Pacher.

Table 1. Dendrochronological dating of spruce wood of the panels "Funeral and Flagellation" (H. Holbein the Elder)

Number of boards	Number of growth rings	Dendrochronological dating from the youngest and the eldest ring
<u>Funeral:</u>		
Board I:	58 growth rings	1477 - 1420
Board II:	37 growth rings	1481 - 1445
Board III:	40 growth rings	1482 - 1443
Board IV:	59 growth rings	1480 - 1422
Board V:	43 growth rings	1481 - 1439
Board VI:	66 growth rings	1478 - 1413
Board VII:	50 growth rings	1481 - 1432
<u>Flagellation:</u>		
Board VII:	50 growth rings	1473 - 1424
Board VI:	36 growth rings	1481 - 1446
Board V:	39 growth rings	1481 - 1443
Board IV:	45 growth rings	1480 - 1436
Board III:	42 growth rings	1481 - 1440
Board II:	45 growth rings	1479 - 1435
Board I:	58 growth rings	1480 - 1423

**Fig. 1 b:** H. Holbein the Elder: "Funeral" (photograph: Fürstenerbergssammlungen Donaueschingen)Fir Wood

Two dating examples will be described using the fir chronology of Becker and Giertz-Siebenlist. The panel "Annunciation" (Master of the Münchener Drachenkampfes, Fürstenerbergssammlungen Donaueschingen) contains two boards with 69 and 78 growth rings. The youngest growth ring had grown in the year 1466. The art-historical attribution was done for about 1460. That means only a small correction to a date some years later had to be done. The panel "Hl. Laurentius" (M. Grünewald, Städelches Kunstinstitut Frankfurt, Fig. 2) contains three boards, but only two boards could be measured. The last ring had grown in the year 1503 and the datation confirms the art-historical attribution.

In this context it must be emphasized that only the last ring available for the measurement can be dated and only a "terminus post quem" for the creation of a panel can be given. A consideration or a calculation about the number of sapwood or cut growth rings as proposed by Neyses (1985) is not possible. It is impossible to estimate how many rings were cut off during the manufacturing process.

Pine Wood

In combination with the establishment of a pine wood chronology for the dating of historical buildings in Northern Germany (Eckstein, Schubert, Klein 1986), it has been possible to date also panels of the church "Peter and Paul" (Hamburg-Bergedorf) showing scenes of the life of Christ and the passion cycle. While 18 panels could not be dated because of tangential boards with only few rings, the 5 other panels originating all from the same tree, contained 145 growth rings dated between 1683 and 1539. The youngest growth ring had grown in the year 1683 and the art-historical attribution to the end of the 17th century can be confirmed.

Conclusion

From the dendrochronological investigations of conifer panels it becomes evident that a "terminus post quem" for the creation of a painting can be determined. An exact dating to the felling year of the tree, however, is not possible because this method is restricted to the last tree ring available for measurement. From the absolute dating of many panels it can be concluded that for making the panels the entire tree radius was often utilized and merely the bark removed. A visible differentiation between sapwood and heartwood of spruce and fir is not given and therefore a calculation for a sapwood statistic is not necessary and not plausible. However, it is indispensable to establish or use chronologies for the different countries and regions, because the growth ring structure of conifer wood changes in dependence of the altitude of forests. The use of dendrochronological analysis for dating different conifer species is possible, but is not applicable to tangential boards with only few rings and small boards with few rings.

**Fig. 2:** M. Grünewald: "Hl. Laurentius" (photograph: Städelches Kunstinstitut Frankfurt)

Literature

Becker, B. and V. Giertz-Siebenlist 1970: Eine über 1100-jährige mitteleuropäische Tannenchronologie. *Flora* 159, 310-346.

Eckstein, D., Schubert, H.-L. and P. Klein 1987: Aufbau einer Kiefernchronologie für Norddeutschland. *Holz als Roh- und Werkstoff* 45, 344.

Klein, P. 1985: Dendrochronologische Untersuchungen an Gemäldetafeln und Musikinstrumenten. *Dendrochronologica* 3, 25-44.

Klein, P. and E. Bock 1989: Abschlußbericht VW-Stiftung "Aufbau von Nadelholzchronologien zur Datierung von Gemäldetafeln und Saiteninstrumenten", unpublished.

Neyses, M. 1985: Dendrochronologische Untersuchungen an drei spätgotischen Bildtafeln eines Marienaltars aus Bernkastel-Kues. *Trierer Zeitschrift* 48, 201-209.

Siebenlist-Kerner, V. 1984: Der Aufbau von Jahrringchronologien für Zirbelkiefer, Lärchen und Fichten eines alpinen Hochgebirgsstandortes. *Dendrochronologica* 2, 9-29.

SUMMARY

Because the interior climate of museums is not constant, paintings with a wooden support change their dimensions. A new automatic measuring system, which allows simultaneous measurements at 60 different places on the wooden panel, was used for registration of the dimensional changes of a panel in Gemäldegalerie Berlin-Dahlem, from September 1988 to June 1989. Through this preliminary test it could be demonstrated that this panel changes its dimension immediately in dependence on relative humidity changes. The investigations will be continued in cooperation with Gemäldegalerie Berlin-Dahlem to analyse dimensional changes as a function of the size of the panel, tree species and the age of the wood.

KEYWORDS

Dimensionstability, measuring system, museum climate, swelling and shrinkage, wooden support.

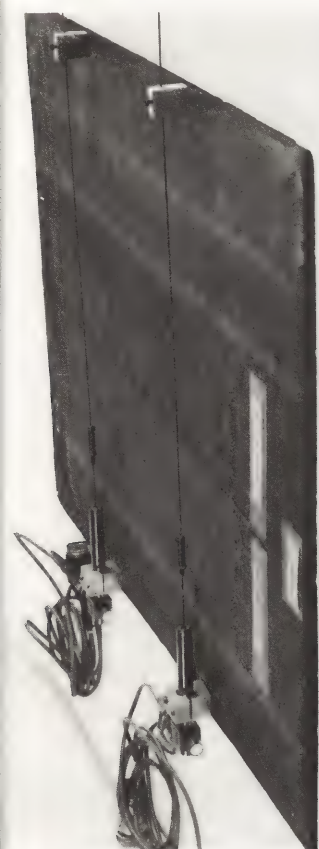


Fig. 1:
Original oak panel with two inductive displacement transducers for measurements in the climate chamber

INVESTIGATIONS ON SWELLING AND SHRINKAGE OF PANELS WITH WOODEN SUPPORT

Peter Klein* and Friedrich-Wilhelm Bröker,
University of Hamburg*,
Federal Research Centre for Forestry and Forest Products
Leuschnerstrasse 91, 2050 Hamburg 80
Fed. Rep. Germany

Introduction

Changes of humidity cause dimensional changes of wooden supports. The order of magnitude of these changes is practically unknown.

In a preliminary investigation a measuring system based on an inductive displacement transducer was tested on two panels of oak wood without a paint layer with automatic data registration. An original 17th century oak panel and a new oak panel with the same size of 500 x 400 x 15 mm and a radial orientation of the growth rings were analysed in a climate chamber. Figure 1 shows the inductive displacement transducer which covers the width of 400 mm. The range of measurement of the transducer is ± 20 mm. The error of measurement is smaller than $\pm 0.2\%$ in relation to the measurement value.

For registration and ranging a channel system UPM 60 manufactured by Hottinger Baldwin Meßtechnik was used.

The recording instrument UPM 60 records simultaneously up to 60 measurements automatically with free selection of time intervals.

This instrument disposes of several different amplifiers, a mini-computer to control the recording of the results, a printer and automatic transfer of the results.

After testing in the climate chamber an oak panel (Portrait of a Man, Joos van Cleve, 1480/85-1540 from Gemäldegalerie Berlin-Dahlem) was analysed with the same measuring system during the period September 1988 to June 1989.

Results from the climate chamber

Daily changes of humidity in the climate chamber ranging from 55 and 85% caused dimensional changes of different extent and velocity on the surface of the two panels (Fig. 2).

The dimensional change on the new panel (1987) was about 800 μm , on the original panel about 600 μm . The differences can be attributed to the different density of the two panels (panel 1987: 0.67 g/cm^3 ; panel 1625: 0.55 g/cm^3). The new and the original panels react in the same manner to humidity changes in the climate chamber.

Results from Gemäldegalerie Berlin-Dahlem

The measuring system of the panels in the climate chamber was transferred to a panel hanging on the wall in Gemäldegalerie Berlin-Dahlem for registration of the dimensional changes of the wood over the whole width at three different positions and on four local positions (width only 20 mm). In addition, the following variables were monitored: interior humidity, exterior humidity, room temperature and the temperature on the backside of the panel at four locations, every 2 hours from September 1988 to June 1989 (Fig. 3).

For comparative assessment of measurements, the new oak panel (1987) was also installed in Gemäldegalerie Berlin-Dahlem.

As can be seen at test points 7 and 8, this oak panel reacts immediately with dimensional changes under changing relative humidity (registration over the whole width).

When relative humidity decreases by 10% (from 60 to 50%) the transverse extension of the oak panel decreases by about 400 μm = 0.4 mm (Fig. 4).

Also at the back of the oak panel "Portrait of a Man (Joos v. Cleve)" dimensional changes of up to 400 μm = 0.4 mm were measured during a period of 9 months (Fig. 5, registration also over the entire measurement range).

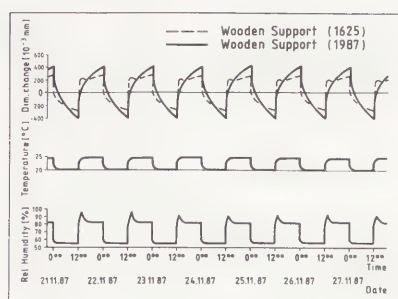


Fig. 2:
Dimensional changes of the wooden support related to daily changes of relative humidity

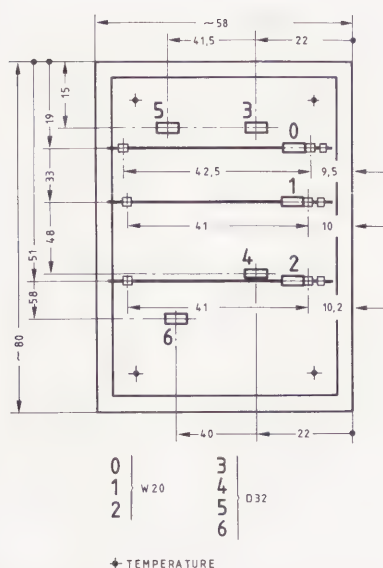


Fig. 3:
Arrangement of the inductive displacement transducer on the original oak panel of the painting "Portrait of a Man"

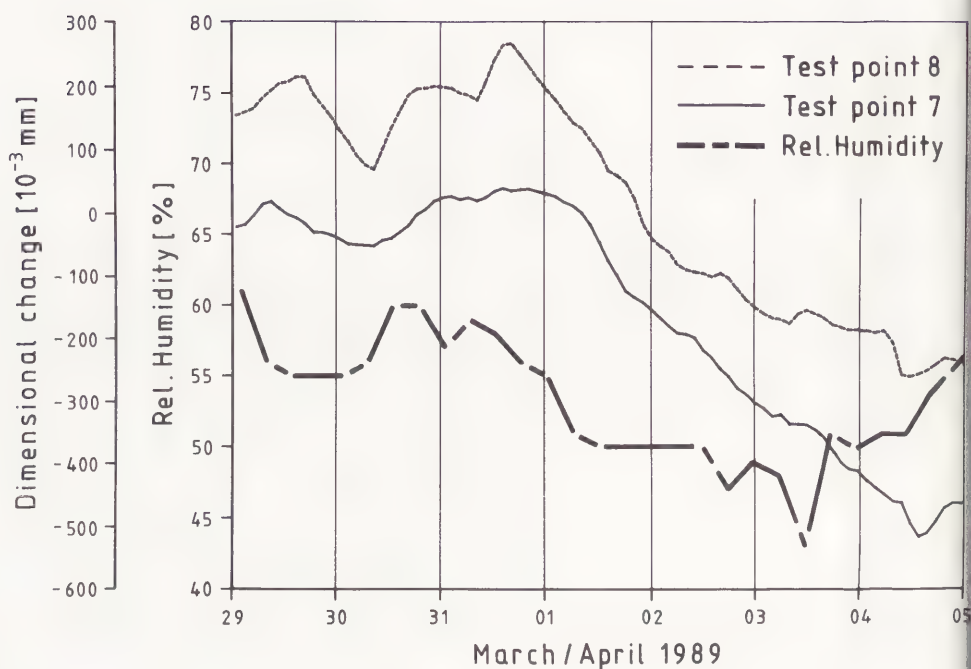


Fig. 4:
Dimensional changes of the new wooden panel (1987) related to the changes of relative humidity in Gemäldegalerie Berlin-Dahlem

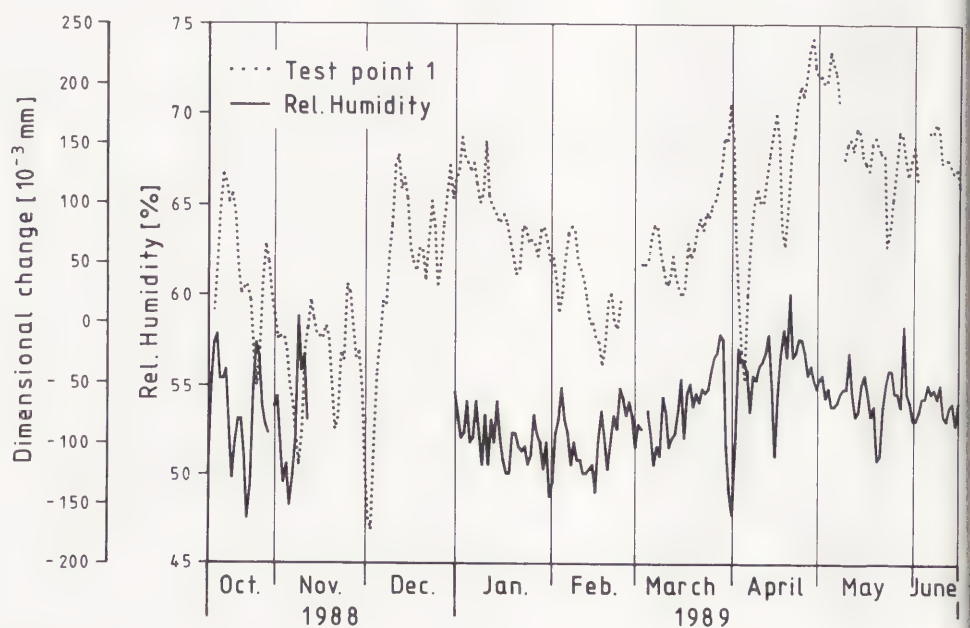


Fig. 5:
Dimensional changes of the oak panel "Portrait of a Man" related to the changes of relative humidity in Gemäldegalerie Berlin-Dahlem

When the results were related to the measurement distances of 400 and 20 mm, respectively, it was found that elongations of up to 0.10% occur at points 0-6 (Portrait of a Man) (Fig. 6, test points 0-2: whole support width, test points 3-6: width 20 mm). Transverse dimensional changes of the new oak panel (1987) varied between 0.15 and 0.17%. The change in humidity was 10%.

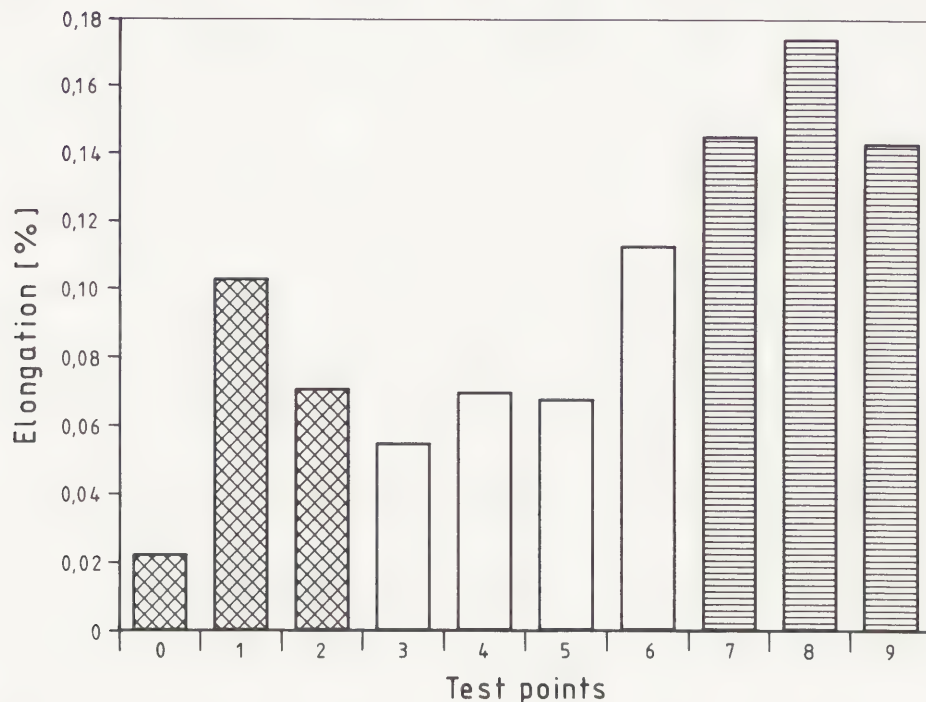


Fig. 6:

Elongation (in %) at different measurement points on the panel "Portrait of a Man" (points 0-6) and on the new oak panel (1987) (points 7-9)

From this test the conclusion can be drawn that large and small transducers produce the same results. Consequently, accurate results in dimensional changes of paintings due to changes in relative humidity can be accurately determined by using small transducers with only 20 mm of measurement length.

Conclusions

The used measuring system clearly shows dimensional changes of oak wood panels. The results refer only to the analysed panels. Panels of different wood species and different construction will be tested in future to demonstrate the dependence of the dimensional stability on species, size and other factors. Besides the dimensional changes of the wood the changes of the paint layer will be tested, too. By comparison of the results from the front and the backside new information will be obtained for the range of climate stability in museums, in exhibitions and for the transport of wooden objects of art. All results refer directly only to the analysed panels; any variation in the wood, knots or variations of growth ring structure or of wood density will cause different results.

Literature

- Agnesi, M. and V. Arrigoni 1973:** Nota sult' applicazione di metodi elettrici al rilievo delle deformazioni di dipinti su tela e su tavola. In: G. Urbani (ed.). Problemi di Conservazione. Edifice Compositori, Bologna, 239-258
- Bröker, F.-W. and P. Klein 1989:** Bestimmung von Flächendehnung bei Gemäldetafeln aus Holz. Holz Roh-Werkst. Berlin, 47, 206
- Hilbert, G.S. 1974:** Untersuchungen des wandnahen Raumklimas in Raum 144 der Gemäldegalerie Berlin-Dahlem. Unpublished manuscript, 7 pp.
- Matejak, M. and E. Popowska 1986:** Wood humidity in the museum rooms SGGW-AR, For. and Wood Technol. 33, 37-41
- Schwarz, A. 1990:** Infrarot-thermographische Dichte- und Feuchtemessungen an bemalten Holztafeln. Holz Roh- Werkst. 48, p. 36

ABSTRACT

This paper examines the problem of visualisation of an X-ray fluorescent image. The main feature of the proposed scheme is the use of the Link System 860-500 or its analogue which is commercially available for energy dispersive microanalysis.

To have the scanning X-ray spot on the surface to be examined the tube with internal electron beam deflection is applied.

This method gives 5-10% concentrational sensitivity for 1-3 hours scanning time presenting some advantages when compared to Neutron Activation Autoradiography.

KEYWORDS

X-ray Fluorescent Imaging, Scientific Examination, Conservation Science, Criminalistics.

THE X-RAY FLUORESCENT IMAGING OF WORKS OF ART

Dr. Alexander J. Kossolapov

USSR, 191065 Leningrad

Dvortsovaya nab. 34

The Hermitage Museum, Lab. Sci. Exam. Works Art

Introduction

Up to the present time, the only method used to visualise the concentrational distribution of a given chemical element on the surface of a painting was Neutron Activation Autoradiography (NAAR). NAAR was first introduced into museum practice in 1968 by E. Seire et al. for paintings examination /1/. To the best of our knowledge, NAAR has since been used only several times /2/ due to some significant inherent disadvantages which make application of the method too complicated. Some of the major disadvantages of NAAR are:

- the necessity for use of a nuclear reactor
- the large dose of radiation needed for activation (several thousand rads)
- the fact that NAAR (using thermal neutrons) is not sensitive for the analysis of lead and iron which are two basic elements of paints
- the concentrational sensitivity is small due to the great magnitude of "noise"-the emission of all chemical elements still active at the time of image registration on the film
- isotopes with long half-life times may appear in some kinds of paints so that an activated painting may remain radioactive for years.

When one considers the underlined drawbacks of NAAR, it may seem desirable to solve the same problem in a more acceptable way.

X-ray fluorescent imaging

The idea of X-ray fluorescent imaging of objects is not new in itself; it is commonly used in scanning electron microscopy of objects (SEM). It follows that one might try to copy the SEM principle using the same kind of spectral selective imaging device but a different scheme of scanning (i.e. the scanning could be exerted on the macro-level instead of the micro-level). For the latter purpose an X-ray tube with internal electron beam scanning is well suited.

The Link System 860-500 /3/ has been used for X-ray fluorescent analysis of art objects in the Hermitage Laboratory since 1987. The System 860-500 was designed by the manufacturer to implement energy dispersive microanalysis in SEM. The Si(Li)-detector (150eV resolution), coupled with a 100MHz ADC and pulse processor, is controlled. The software includes the collection, visualisation and processing abilities for 128x128 images collected in the fluorescence of an arbitrarily chosen group of periodic elements. The one pixel signal collection time (scanning constant) may be varied from 1msec to 8sec. The corresponding deflection step-voltage is internally generated to control the SEM electron beam deflecting windings.

The portable X-ray source REIS-1 /5/ operating at 5W electric power (10-50kV, 100mA) was chosen to excite fluorescence of the object. The standard REIS tube was replaced with a tube specially manufactured to permit internal electron beam scanning. The scanning was controlled by means of the System generated step voltages amplified to several Amperes current in order to feed the TV-monitor type's electromagnetic deflection windings.

With the tube's target size of 24x24mm (d=36mm) and a focus size of less than 0.2mm, one can achieve approx. 120x120 pixel spacial resolution on the target and, consequently, on the scanned object. This is quite satisfactory because 128x128 pixel image is inherent for the Link System 860-500.

The principal scheme of the whole device is given (see Fig.1).

The size of the scanned picture is appr. 60x60mm with a scanning spot diameter of 0.5mm. Operating the spectral channel at a pulse-processing constant time of 10mcsec permits one to pipe 5000-6000 counts/sec through it. By choosing a scanning rate of 200 msec/pixel (i.e. 55 min per the whole raster, one might expect to accumulate appr. 1000 counts per pixel. This is enough for reliable registration of $(3\sqrt{1000/1000})=9.5\%$ difference in the concentration of the chosen element. By setting a scanning rate of 600msec/pixel (appr. 3 hours per raster), a concentration sensitivity of 5.5% may be reached.

Prospects

The device outlined in Fig.1 can be easily made in any laboratory that is equipped for energy dispersive X-ray fluorescent analysis (SEM, Electron Microprobe). For the more advanced institutions that have a good technical base some other means might appear more promising. One proposition is the construction of a computerized system using a proportional X-ray detector and an optical scheme of the camera-obscura* type. Balanced differential elemental filters could be applied for spectral selection. The presence of a modern computer in the system would permit one to use a quite large aperture, the following computer correction of the image would produce good resolution. The use of a proportional X-ray detector is essential due to its capability to register high count rates (up to 100000 counts/sec) and so to achieve a good sensitivity of the tool.

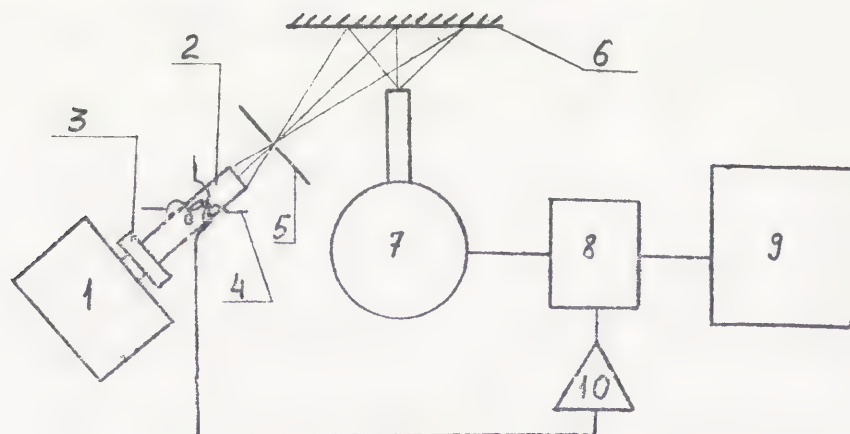
Experiments with the camera-obscura, differential filters and X-ray image amplifiers could also be considered.

Conclusions

The method of X-ray fluorescent image visualisation may be applied in the scientific examination of works of art when the optical contrast is not enough to reveal a given detail in any optical region (Infrared, UV-reflectance or in optical range luminescence).

X-ray fluorescent image visualisation may be applied for reading details on paintings, papers etc. made of a material that differs in any periodical element concentration from the one in the surrounding area of the object. The said details in practice may be signatures, inscriptions, restoration overpaintings, traces of missing metal inlays on art objects etc.

Fig.1 The scheme of X-ray fluorescent imaging.



- 1.X-ray source REIS. 2.X-ray tube with internal electron beam scanning. 3.The focusing magnet. 4.X-Y deflection windings. 5.Lead screen with an aperture. 6.Object for imaging. 7.Si(Li)-detector. 8. 100MHz ADC + Pulse processor, coupled with computer. 9.Colour monitor. 10.Deflecting current amplifier.
Pos.7,8,9 are the standard set of Link System 860-500 for energy dispersive X-ray microanalysis.

* Camera-obscura here means a device for object imaging using a small aperture. Camera-obscura is a photographic term which was introduced by Galilee.

Notes.

1. E.V. Sayre, H.N. Lechtman "Neutron Activation Autoradiography of Oil Paintings", Studies in Conservation 13, no.4 (1968); 161-185.
2. C-O. Fischer et al. "Grundlagen der Neutronenaktivierungs-Autoradiographie und -Analyse" Symposium Zerstörungsfreie Prüfung von Kunstwerken, 19./20.11.87, Berlin, pp.87-96.
3. System 860 Series 2 Energy Dispersive Microanalysis, Link Systems Ltd. Halifax Rd., High Wycombe, Bucks, HP 12 3SE, England
4. Alexander J. Kossolapov "Historical and Material Aspects of Wood Gilding in Russia. Icons" (Paper delivered at the First International Gilding Conservation Symposium, Philadelphia Museum of Art, Philadelphia PA, 26-28 October 1988. To be published.
5. Portable X-ray Source REIS, (USSR, Leningrad, Prod. Amalgam. "Svetlana", 1986 (in Rus.)).

ABSTRACT

Investigation was carried out on different kinds of protein glues: restoration hide glue obtained from tanned calf leather, and sturgeon glue. Such parameters were studied as strength and maximum permissible deformation during mechanical testing of films. Comparative analysis was done of properties of glues under investigation such as: appearance, development and subsequent relaxation of inner tensions springing up in glue joints when water evaporates in the course of the formation of a glue joint, properties which are of paramount significance in restoration practice. Investigation was also carried out on the properties of leukases prepared with different protein glue solutions. Molecular mass distribution of protein glues under investigation was determined on polyacrylamide gel plates by means of electrophoresis.

KEYWORDS

Glue, protein, mechanical properties, relaxation.

INVESTIGATION OF PROPERTIES OF PROTEIN GLUES

E.A. Luybavskaya, Cand. of Chem.
10 Krestyanskaya Pl., Moscow
VNIIR
U.S.S.R.

Introduction

Animal glue still has to be used in national economy nowadays, in spite of an intensive development of synthetic glues. Special quality fish glue made of skin of sea fish: cod, shark, is widely used in electronic industry to manufacture coloured TV tubes. Glue made of swimming bladders of sturgeon and sheat-fish is used in restoration and food processing industry. In addition to the above listed glues, hide glue, made of tanning industry waste and various brands of gelatine, is at present manufactured by factories. The principal component of any animal glue, determining its gluing capacity, is glutin formed when collagen is treated with hot water. Gelatinous glues have long been used in restoration practice. They attract restorers because they are not toxic, convenient in use, and have high gluing capacity. Glues of this group do not dissolve and swell in organic solvents, which is important in restoration practice. The most significant technological property of animal glues, which no other glue has, is the capacity of their hot solutions, when their temperature drops by just a few degrees to form a thick jelly, and to melt again when the temperature rises. The ultimate strength of sturgeon glue constitutes 103 Pa. These glues have, however, their own limitations. Their limitations do, first of all, include high hydrophilia, and, secondly, their possible biodegradation. In unfavourable conditions glue lines are capable of absorbing 800-900% of moisture, and if moisture content in glue is 20% or more, it loses its strength, and conditions are created for biodegradation. With less than 10% moisture content a glue joint becomes brittle. The optimum water content in glue is 14%. Irreversible ageing processes occur in glue films in the course of their being used. In so doing, strength properties worsen, and glue joint brittleness rises. Such properties of sturgeon glue as extreme, and not always required, strength, brittleness and high solution viscosity compel restorers to seek possibilities of changing the property of sturgeon glue towards less viscosity and making its films more elastic. For these purposes one can employ such methods of plastification as adding honey, polyvinyl alcohol or their mixture to sturgeon glue. Such plastification does not always have, however, the desired effect. When working in the archives of the Moscow Kremlin Armoury and studying (the 18th century) ledgers of the Cyril Byelozersk Monastery it was found that hide, or leather, glue was used in making icon leukases. The entire amount of documents reflecting the activities of icon leukas makers and their consumption of materials show that hide glue was chiefly used to make up icon ground coating. There were virtually no exceptions to this practice. Hide glue was often used also to "repair" icons, i.e. for their restoration. We had a task to work out methods of making a high quality restoration hide glue and to investigate the properties of both sturgeon and hide glues, and to compare them. Investigations and technological works, carried out in the VNIIR Tempera Painting Restoration Department, made it possible to manufacture now industrially a special restoration hide glue. The raw material for making restoration hide glue is calf dermis. The raw material, ground, thoroughly washed and neutralized, is boiled in distilled water. The glue broth goes through a precipitation stage of globular proteins, worsening the gluing properties, then filtration and after that is subjected to vacuum drying. Powder-like dry hide glue, obtained as a result, is well soluble in water when heated. We should like to emphasize that factory-made restoration hide glue surpasses, in its degree of purification, the glue obtained previously in laboratory conditions. When studying and comparing the properties of hide and sturgeon glues, we investigated the kinetics of growing and relaxing tensions, appearing in the glue when water evaporates and the glue layer hardens. This parameter is important for restoration materials, as a material, manifesting high inner tensions when forming a coating or glue joint, can damage the object of restoration.

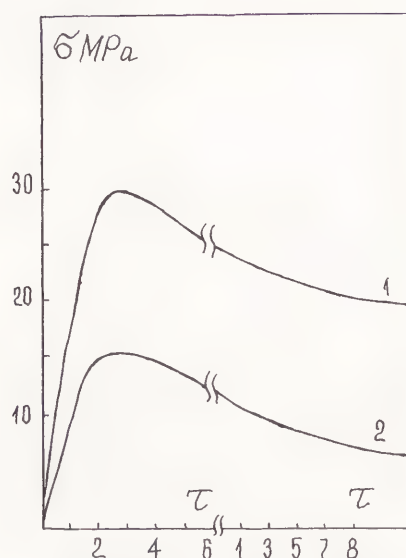


Fig. 1 Dependency of inner tensions in hide glue films.
curve 1 - sturgeon glue
curve 2 - hide glue

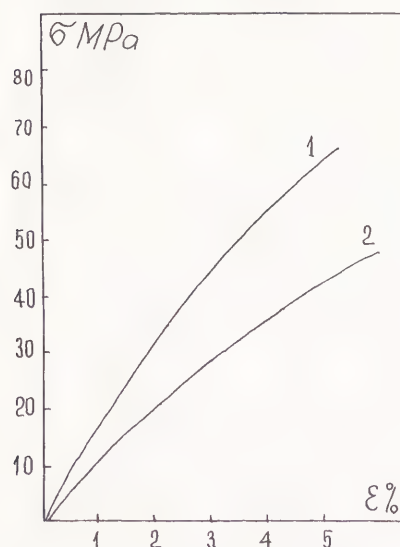


Fig. 2 Deformation curves of sturgeon and hide glue films.
curve 1 - sturgeon glue
curve 2 - hide glue

We chose two independent methods of estimating this parameter: a polarization optical method and a mechanical cantilever method.

The polarization optical method made it possible to determine not only the maximum values of tensions that spring up, but also to reveal slow processes of relaxation of inner tensions.

The principal parameters investigated coincide when applying the two methods, which allows to consider the two methods precise and reliable, and the values of maximum inner tensions, determined by them, true.

Fig. 1 represents curves expressing the dependency of inner tensions, that spring up when sturgeon and hide glue films are formed out of 5% water solutions, on time.

The graph shows that the highest rise in inner tensions of the glues investigated was observed in the first 2-3 hours of drying, in so doing the maximum, very high, value of this parameter: 30 MPa for sturgeon glue solution, was observed one hour, or an hour and a half, after hardening had begun, and lesser values for hide glue: 18 MPa, were observed 2-3 hours after the process had begun.

The character of growing inner tensions at the first stage of hardening was the same for the two glues; these parameters of hide glue were, however, substantially lower by absolute value. Within four days tension in a sturgeon glue film dropped from 30 down to 20 MPa, and in hide glue this change constituted half this value, approximately 10 MPa.

Physico-mechanical methods of investigating films of these glues are of great practical significance when studying and comparing the properties of sturgeon and hide glues. The testing was conducted by means an "Instron" tensile-testing machine.

Fig. 2 represents deformation curves of sturgeon and hide glue films. These investigations showed that the mechanical strength and elasticity of sturgeon and hide glues are close to each other and differ only slightly: tensile strength of hide glue is 15-20 MPa lower, and maximum permissible deformation is 2% higher than these values of sturgeon glue films.

We also studied changes in linear dimensions depending on temperature by UIP-65 capacity dilatometer. As can be seen from Fig. 3, linear dimensions of films of glues under investigation diminish when heated from 25 to 100°C. With further heating up to 140°C no changes in linear dimensions were observed.

Fig. 3 shows that linear thermal compression coefficient of sturgeon glue films is much higher than that of hide glue. It agrees quite well with values of inner tensions, springing up in glutinous glues, obtained by us earlier.

Sturgeon glue, whose films have big inner tensions, has also a much larger linear thermal compression coefficient.

Viscosity of water solutions of these glues was studied; to do so we employed a standard technique of determining glue viscosity in Engler degrees. Viscosity of 5% sturgeon glue solution constitutes 78°E, and viscosity of 5% hide glue solution constitutes 40°E, i.e. half as much. Consequently, hide glue solution has greater penetrating capacity owing to lesser solution viscosity.

Properties of leukases, made on hide and sturgeon glues, were investigated for a more complete study of hide and sturgeon glue properties.

Fig. 4 represents characteristic curves of changes in inner tension in leukas made on 5% sturgeon and on 5% hide glue solutions. Similar characteristic curves were obtained for leukases made on solutions of different concentrations, e.g., 10%.

Characteristic curves represented show clearly that leukas on sturgeon glue, when water has been evaporated and it has hardened, reveals higher absolute values of inner tensions. The difference of maximum values of inner tensions reaches 10 MPa, and, if tension in leukases on hide glue disappears 10 hours after drying has begun, tension in sturgeon glue leukas of about 2-3 MPa remains for up to 3-4 days.

Thus, sturgeon and hide restoration glues, being protein glutinous glues and having close mechanical properties of free films, are distinguished by absolute values and character of relaxation of inner tensions appearing when film coatings are being formed, both pure and mixed with chalk (leukas).

Sturgeon glue and leukas based on it reveal higher inner tensions (20 MPa), and hide restoration glue and leukas based on it have much lesser absolute values of inner tensions (10 MPa) and relaxation of tensions is more uniform in character.

Sturgeon and hide restoration glues are distinctive also by the value of viscosity of water solutions of equal concentration, in so doing viscosity of hide glue is half as much as that of sturgeon glue.

In order to investigate the molecular mass distribution of different kinds of hide glue (depending on the temperature of boiling) and that of sturgeon glue, we made, jointly with the En-

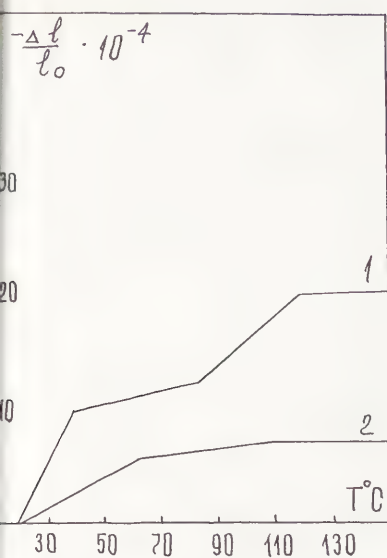


Fig. 3 Linear dimensions of films of glues.
curve 1 - sturgeon glue
curve 2 - hide glue

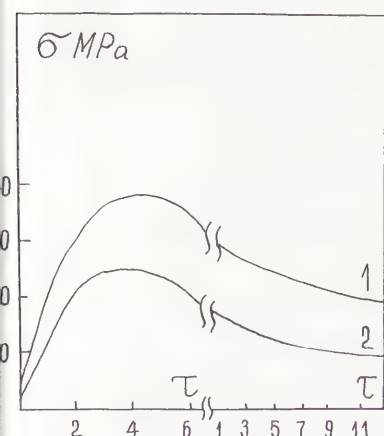


Fig. 4 Changes in inner tension in leukas.
curve 1 - for leukas made on sturgeon glue
curve 2 - for leukas made on hide glue

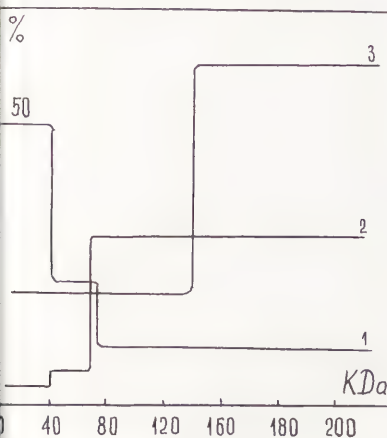


Fig. 5 Molecular mass distribution of glues.
histogram 1 - low viscous hide glue
histogram 2 - highly viscous hide glue
histogram 3 - sturgeon glue

gelhart Molecular Biology Institute, a determination of molecular masses by electrophoresis method in polyacrylamide gel. For this purpose electrophoresis was made of protein glue samples in 10% polyacrylamide gel of the following composition:

12.5 ml - Stock
18.75 ml - 1M TRIS HCl pH 8.8
.2 ml - 25% SDS
.2 ml - 10% persulphatammonia
up to 50 ml - H₂O.

Protein separation in PAAG with Na dodecylsulphate was made by Lemme method. Glue samples were diluted with distilled water to 1 mg/ml protein concentration. The separating PAAG was prepared on .375 M tris - HCl buffer pH - 8.9; the concentrating 4% PAAG, on .125 M tris - HCl pH - 6.9. Electrode poiser: .025 M Tris - (oximethylaminomethane) and .196 M glycine. All buffers contained .1% ADC - Na. Separation was made on 20 by 20 mm, 1.0 mm - thick plates.

Samples, before being introduced into gel pockets, were treated with 2% sodium dodecylsulphate in .065 M tris - HCl pH - 6.9 with 1% - marcaptoethanol, .08% blue bromophenol and 10% glycerine, and incubated for 2 minutes at 100°C.

Separation was made at 400 volts (20 volts per 1 cm) potentials difference on the plates till blue bromophenol reached the plate edge. Gel was washed in 20% trichloroacetic acid (TCA) twice for 30 min and dyes for 6 hours with .4% R-250 "Serva" kumassi in 20% isopropanol and 10% acetic acid.

All the samples under investigation (Fig. 5) demonstrate a different distribution pattern by molecular masses. As can be seen from Table 1 and the histogram (curve 1), low viscosity glue is characterized by components with the molecular mass up to 43 kiloDaltons (54.5%), fraction with the molecular mass of 43 to 73 kDa constitutes 21.9%, one with 73 to 150 kDa, 10.3%, and one with molecular mass of over 150 kDa, 12.5%.

Curve 2 in Fig. 5 represents a histogram for a highly viscous hide restoration glue. Unlike low viscous hide glue, its fraction with a 43 kDa molecular mass constitutes 22.4%, components with a 43 to 73 kDa molecular mass constitute 22.1%, those with a 73 to 150 kDa molecular mass constitute 20.5%, and fraction with the largest molecular mass, over 150 kDa, constitutes 35.3%.

Curve 3 shows the molecular mass distribution of sturgeon glue. Highly molecular fraction with an over 150 kDa molecular mass constitutes 58%. Low molecular fraction (43 to 73 kDa molecular mass) constitutes just 9%.

Table 1

Distribution of Glue Components by their Molecular Masses

Glue (fraction	0-43 kDa	43-73 kDa	73-150 kDa	over 150 kDa
Low viscous	54.5	21.9	10.3	12.5
Highly viscous	22.4	21.1	20.5	35.3
Sturgeon	2.3	6.8	33.3	57.9

Conclusion

The investigation carried out leads to the conclusion that a substantial difference in physico-mechanical properties of glutinous glue, observed in restoration practice and revealed previously by our researchers, is caused by different molecular mass distribution. The largest (in percentage) share of highly molecular fraction is contained in sturgeon glue solution, which accounts for its high structural viscosity, exceptionally great mechanical strength of glue joints (on the level of epoxide resin), low plasticity and brittleness of hardened films. Highly viscous hide glue also contains molecular mass fraction of over 150 kDa, but in a substantially less quantity (35.3%). Other protein fractions, constituting highly viscous glue, have lower values of the molecular mass. One may suggest, by way of a hypothesis, that while highly viscous hide glue is hardening in the course of the formation of a glue joint, highly molecular fraction forms a peculiar carcass ensuring sufficient strength of the glue joint.

One may suggest too that the role of fraction with a lesser molecular mass consists in the plastification of highly viscous hide glue and in diminishing the structural viscosity of its water solutions.

Low viscous hide glue contains mostly fractions with a low molecular mass, which is, evidently, the reason for low viscosity of its water solution, an exception, an exceptionally great penetrating capacity and lesser strength of glue joints made by it.

In the VNIIR hide glue has passed from an experimental testing stage to restoration practice. Hide glue was used in 1984 for an emergency reinforcement of icons of Novgorod St. Sophia Cathed-

dral, which was required in connection with the dismantling of the iconostasis and its altered storage conditions.

Bibliography

Luybavskaya E.A. Examination of glutinous glues. Culture and Art in the USSR. ISSN 0233-8491. Express Information, vol. 6, M., 1985, p. 6-10.

ABSTRACT

Noble metal alloys on ivory, historic parchment scripts and precious oil paintings were examined nondestructively on air by the combined PIXE/PIGE method using a 4 MeV external proton beam. Composition results of alloy analysis were unambiguous. Problems in coordinating chromophoric elements arose for unique paintings with a limited pigment palette. Cross sections and X-ray-photo studies in accessible regions of the objects complemented the ion beam results.

KEYWORDS

PIXE/PIGE-examination
nondestructive analysis
pigment analysis
paintings (Caspar David
Friedrich)
gold alloys on ivory
parchment

NONDESTRUCTIVE MULTIELEMENT ANALYSIS OF ART OBJECTS - OPPORTUNITIES FOR THE APPLICATION OF THE EXTERNAL PIXE/PIGE TECHNIQUE

Christian Neelmeijer*, Hans-Peter Schramm**, Helmut Matthes*, Christine Wendt***

* Central Institute for Nuclear Research Rossendorf, PF 19
Dresden, DDR-8051

** Academy of Fine Arts, Güntzstrasse 34, Dresden, DDR-8019

*** National Art Museum "Grünes Gewölbe", Georg-Treu-Platz,
Dresden, DDR-8010

1. Introduction

Restorers, art scientists and criminal officers are interested in investigations of art object substances. The combination of PIXE/PIGE (particle induced X-ray and Gamma-ray emission /1-4/) enables a simultaneous analysis of nearly all chemical elements independently on their bond state. Using an external ion beam /5/ the non-destructive PIXE/PIGE diagnostics on air offers such significant advantages as the following:

- No sample preparation is necessary. Any intact objects or miniatures such as metallic ornaments, glass objects or paintings, historic parchments and pigments of oil paintings may be analyzed.
- High lateral resolution allows for a variety of point studies (about 1 mm² area) of one object or detailed examinations of similar objects for comparison.
- Semiquantitative multielement analysis distinguishes between main and secondary components (as well as trace impurities) with high speed, slight particle irradiation and simple data processing.

Disadvantages of ion beam methods are the following:

- The limitation on mobile art objects, because the territorial position of the particle accelerator is fixed.
- It is impossible to clarify chemical bonds to be necessary for a complete pigment analysis.
- The integral registration of signals arising from elements which are localized at different depths; heavy ions of about 1 MeV/nucleon energy may be helpful.

To interpret the results of PIXE/PIGE measurements on complex material structures, additional tools such as cross sections, XRD- and IR-analysis are often necessary. However, these techniques usually require special sample preparation.

In the past three years the 5 MV Tandem accelerator at the Central Institute for Nuclear Research Rossendorf has been used to study various art objects using a 4 MeV external proton beam. Material studies range from noble metal alloys and stained framed objects to medieval parchment manuscripts and precious paintings.

2. Experimental Conditions

A schematic drawing of the external beam arrangement is given in Fig. 1. The well-collimated proton beam of 4 MeV energy (E_0) passes through a HAVAR exit foil of 2 μ m thickness /6/. Outside the vacuum channel, a nitrogen or helium gas jet /7/ envelopes the projectiles to minimize energy losses and beam divergence, and prevents parasitic X-radiation arising from interactions with atmospheric Ar or Xe atoms. About 1-2 cm behind the HAVAR foil the diagnostic object is positioned and cooled by the gas stream during proton irradiation. X-rays are measured at 135° backward angle by means of a Si(Li) detector of 170 eV energy resolution. Gamma-radiation used for light element analysis ($Z < 14$) is detected by positioning a Ge(Li) spectrometer at the object backside. The number of impinging protons was checked by charge collection at the insulated HAVAR foil.

To ensure a safe nondestructive analysis with statistically significant results for the objects, each type of measurement is accompanied by an compromise of both the allowed ion beam current density and the number of impinging particles. Estimations, registration of reaction temperatures bombarding special paper indicators, thermoelectric measurements and preliminary experiments on adequate test samples helped to determine suitable irradiation parameters. Using a 2 mm² beam spot, beam currents below 10 nA and

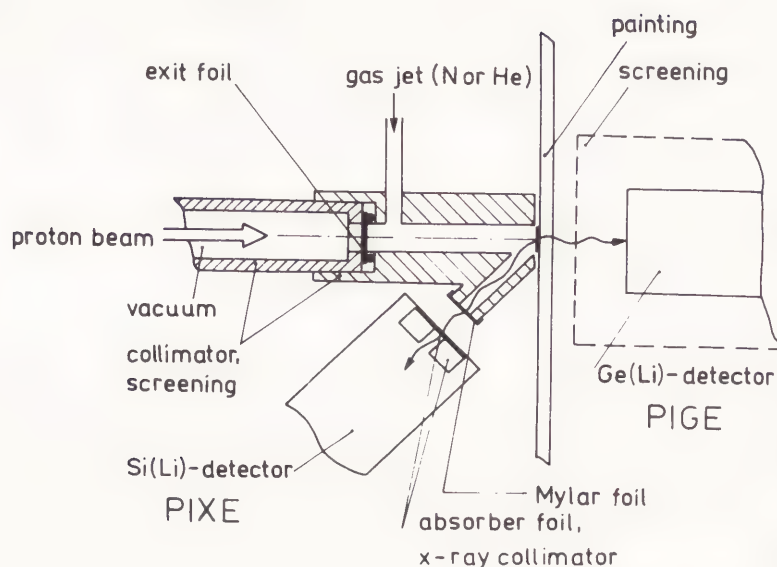


Fig. 1: External beam experiment (schematically) at the 5 MV Rosendorf Tandem accelerator

50 nA correspond to temperatures lower than 20°C and 40°C, respectively. However, bombarding the varnish coating ($C_{30}H_{50}O_2$) of an oil painting for 30 seconds under these irradiation conditions causes a visible darkening. Adequate experiments with polymer foils /8/ resulted in collision-induced broken chemical bonds (C-H-O) accompanied by hydrogen losses via diffusion. Irreversible modifications of varnish-coated paintings can be avoided with high reliability by using 4 MeV protons, 0.5 nA/mm² current density and 30 s irradiation, i.e. 60 mWs/mm² energy deposition.

A distinct lower damage sensitivity has been observed when irradiating organic materials like ivory and papyrus ($E_p = 4$ MeV, 1 mm² spot size, 2 min irradiation). Until now, safe upper limits of the beam current have not been determined because 10-20 nA was found to be sufficient current density for our analytical work. It seems that radiation damage to this type of material is much more related to thermal effects, and cannot be attributed to collision-induced displacements, in contrast to polymer compounds. Metallic compositions like gold and silver alloy ornaments or inlays produce high X-ray yields at some nanoamps proton current.

To exclude superfluous irradiation, the particle beam is automatically stopped when the measurement finishes. A precise and reproduceable positioning of the art objects is ensured by a polyester foil which allows both beam spot fluorescence and position marking.

3. Results and examples

The following three examples will demonstrate the power of the external PIXE/PIGE method; both advantages and limits will be discussed.

- Gold alloys on a historic ivory box (10th century).
- Pigments and stained areas of an old parchment script ("Sachsen-spiegel" (14th century).
- Oil paintings of Caspar David Friedrich: "Zwei Männer in Betrachtung des Mondes" (1819/20) and "Gebüsch im Schnee" (1828).

Extensive studies of an intact medieval altar-piece by the authors have already been reported /9/.

Gold alloys on ivory

Rich carvings on a historic ivory box (10th century) represent the 12 apostles under collonades which are surrounded by a variety of engravings. The nimbus and attribute of each apostle, as well as base and capital of the columns, are decorated with gold alloys. Some engravings show residues of gold inlaid work. Knowledge of the composition of these ornaments combined with the trace analysis results will add to the known history of the art object, and enable the substitution of details which are now lost.

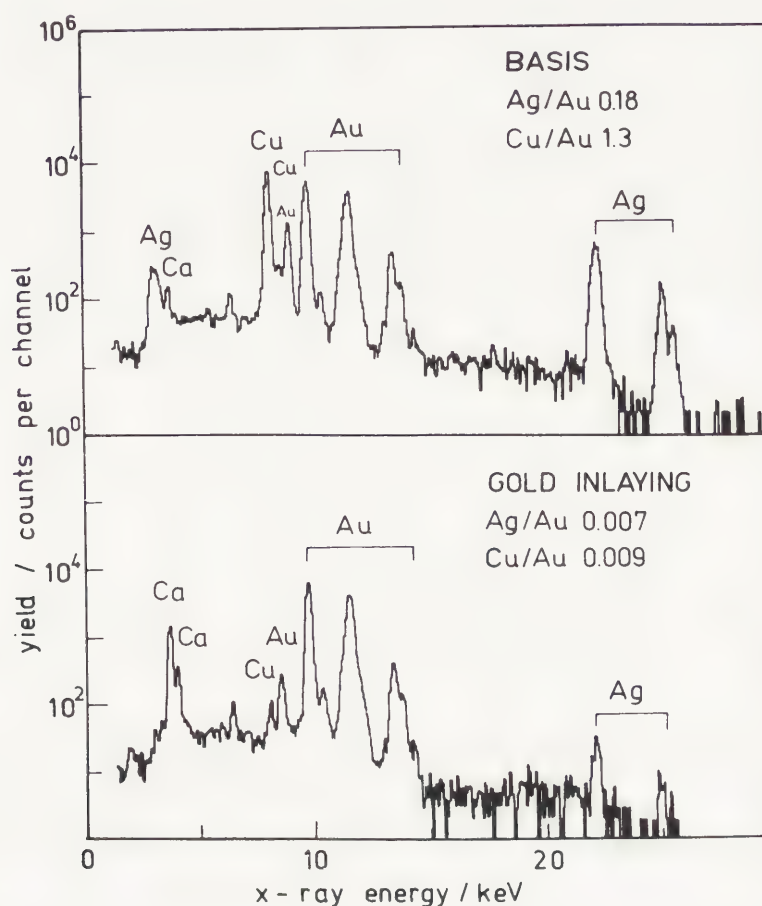


Fig. 2: Typical X-ray spectra of gold alloys on ivory - basis of column and gold inlaid work. The ratio of counts ($\text{Cu-K}\alpha$, $\text{Ag-K}\alpha$, $\text{Au-L}\alpha$) characterizes the composition of the individual alloy.

As shown in Fig. 2, relative intensities of $\text{Au-L}\alpha$, $\text{Ag-K}\alpha$ and $\text{Cu-K}\alpha$ X-radiation were obtained from the measured spectra ($E_p = 4 \text{ MeV}$, $I = 2\text{--}15 \text{ nA}$, 1 mm^2 spot size). Counting rates below 1000/s were adjusted using an X-ray collimator of 1 mm diameter with a 100 μm Mylar absorber to limit pulse pile-up. The spectra show gilts of different qualities. Especially the inlays consist of quasi-pure gold. Base and capital materials of the columns differ whereas the same type of ornament consists of one and the same gold alloy. Traces of gold, copper, iron and manganese were observed on the engravings (Fig. 3). The Fe and Mn impurities possibly originate from tools employed in the past to remove the gold inlaid work. X-radiation peaks from silver components are missing in the trace element spectra because of the relatively low Ag-K X-ray cross section /10/.

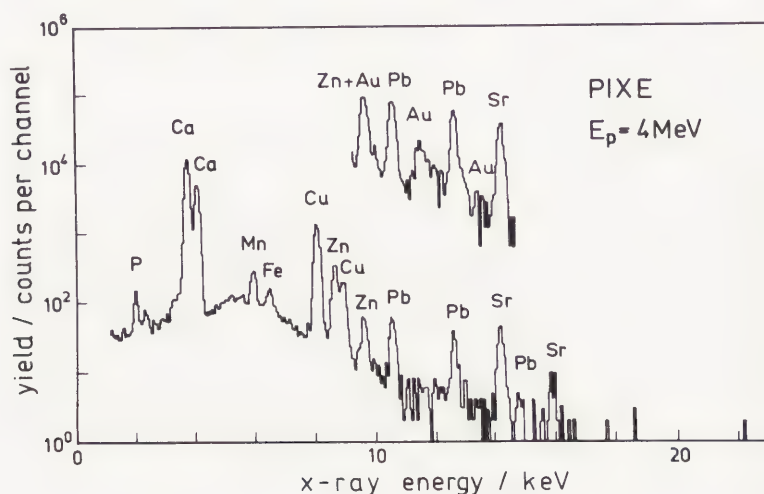


Fig. 3: X-ray spectrum of the pure ivory material (matrix background). The inserted sub-spectrum shows Au-L radiation when bombarding special ivory engravings; this confirms the hypothesis of removed gold inlays.

**Parchment script "Sachsenspiegel" - Justice book (14th century/
Eike von Repkow)**

A generally well-preserved exemplar of the "Sachsenspiegel" justice book deposited in the library "Sächsische Landesbibliothek Dresden" consists of 92 half paged written and painted parchments. Compared to a facsimile print of 1902, some green details have changed on originals to brown, and several areas of damages caused by moisture (water stains, area browning, partial ink-script penetration to the parchment reverse) became visible as a result of war-conditioned storage.

The purpose of the PIXE/PIGE studies of the damaged parchment areas was to determine if the formerly green and now browned details still contain copper; if so corrosion processes ("Kupferfrass" /11/) may be active. Moreover, the chemical explanation for large-area colour changes obvious on some pages was of interest.

The PIXE spectra show that the very high intensities of Cu-K α radiation bombarding undamaged green pigments decrease by more than an order of magnitude for both browned details and faded greens due to water damage.

Besides copper X-radiation, the PIXE spectra of water damaged areas of the parchment contain significant Fe, Zn and Mn peaks: it is possible that pollutions of the water causing this damage deposit these elements on the pure parchment. However, it is of interest to mention an analysis of the illustrations and the ink-script, showing that the maximum Fe, Zn and Mn X-ray yields are observed in the case of green colour. The presence of Si gamma-radiation in the PIGE spectrum of nondamaged green details makes it more difficult to decide whether water impurities (Mn, Fe and Zn) are preferentially trapped in pigment materials, or if green earth with verdigris /12/ had been used.

**Paintings "Zwei Männer in Betrachtung des Mondes" (1819/20) and
"Gebüsch im Schnee" (1828) / Caspar David Friedrich**

The aim of these studies was to gain some fundamental knowledge of the pigment palette of Caspar David Friedrich. Fig. 4 presents typical X-ray spectra. Besides Ca (ground layer - CaCO_3) and Pb (white lead - $2 \text{PbCO}_3 \cdot \text{Pb(OH)}_2$), the element Fe dominates in the spectrum due to the presence of earth pigments /12/.

To supplement the PIXE results, cross section examinations obtained from a negligible particle of the ground layer material revealed a two-layer structure of ground layers which was common to both paintings - chalk ground with yellow ochre, overlaid with white lead containing small amounts of ochre. The intermediate layer of white lead explains the generally observed pure contrasts of X-ray photographs taken from paintings of Caspar David Friedrich.

In the case of "Zwei Männer in Betrachtung des Mondes", the blue pigment of the figures coats and the barrettes consists of Prussian blue ($\text{Fe}_4[\text{Fe(CN)}_6]_3$), and the green pigment of several grass areas is a mixture of Prussian blue and yellow ochre ($\text{Fe}_2\text{O}_3 \cdot n \text{H}_2\text{O}$). The bright crescent is an omission; only the ground with an additional thin layer of white lead is obvious from the X-ray patterns.

As deduced from the PIXE spectrum (insert of Fig. 4), the sky of the painting "Gebüsch im Schnee" consists of cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) mixed with white lead. The simultaneously measured PIGE spectrum contains the expected characteristic Al gamma-radiation. Again the green pigment is Prussian blue with yellow ochre; yellow details contain yellow ochre and all white lights consist of pasty lead white.

After proton bombardment the well varnished surfaces of the paintings showed absolutely no visible changes. Hence the external beam method is suitable to make comparison measurements on art objects which require nondestructive analysis to clarify uncertainties in their composition. In this sense the external PIXE/PIGE technique possibly may be able to offer valuable complementary evidence in the well-known controversy between experts of the two nearly identical paintings "Winterlandschaft" of Caspar David Friedrich (original in London and a "secondary version" (1811) in Dortmund, or reverse ?) /13/. The PIXE/PIGE combination may reveal the presence of analogous or even different paint materials corresponding to the traditional palette of a certain master /14/.

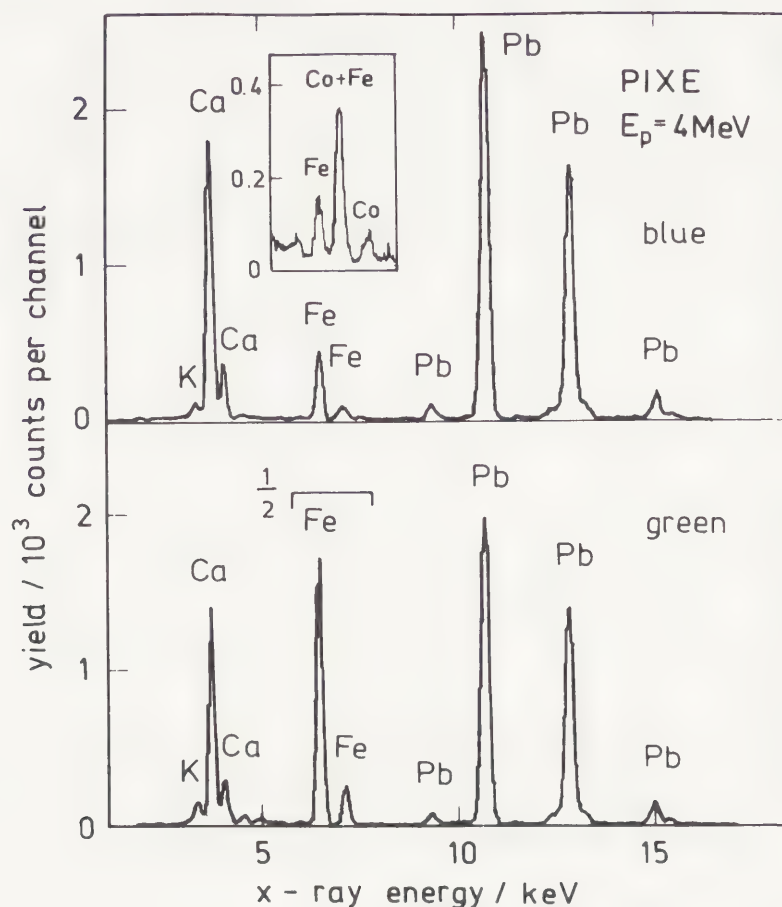


Fig. 4: X-ray spectra of blue and green pigments analysed from the painting "Zwei Männer in Betrachtung des Mondes" of Caspar David Friedrich; the presence of Prussian blue and Prussian blue + yellow ochre (mixed with white lead) was deduced.

Insert: For comparison, the X-ray sub-spectrum taken from blue pigment of the sky ("Gebüsch im Schnee", Caspar David Friedrich) indicates the presence of cobalt blue (white lead) pigment.

4. Conclusions

The combination PIXE/PIGE can be successfully applied to the non-destructive multi-element analysis of art objects.

As demonstrated in this article, metallic alloys were analyzed unambiguously; the identification of elements on parchment allowed deductions of the compositions of paint and script substances to be made; detection of additional foreign elements penetrating the parchment during the war-conditioned storage was also possible.

When investigating paintings, the major problems lie in the interpretation of the measurements. Difficulties in coordinating chromophoric elements arise in the case of unique objects with a very limited pigment palette, as in the case of Caspar David Friedrich, and additional knowledge from other diagnostic methods was indispensable.

Ion beam analysis of organic objects, and inorganic substances embedded in organic materials requires a careful choice of experimental conditions. Varnish coatings especially withstand only very low beam current densities. In such cases the combined PIXE/PIGE technique avoids multiple ion bombardment.

References

- /1/ G. Amsel, Ch. Heitz, M. Menu: MeV ion beam techniques: An outline. Nuclear Instruments and Methods B14 (1986) p. 30
- /2/ F.-W. Richter: Experimental arrangements for PIXE analysis. Nuclear Instruments and Methods B3 (1984) p. 105
- /3/ A. Anttila, R. Hänninen, J. Räisänen: Proton-induced thick-target gamma-ray yields for the elemental analysis of the

- Z = 3-9, 11-21 elements. Journal of Radioanalytical Chemistry 62 (1981) p. 293
- /4/ M. Peisach, D. Gihwala: The determination of minor elements in steel by proton-induced prompt gamma-ray spectrometry. Journal of Radioanalytical Chemistry 61 (1981) p. 37
- /5/ J. Räisänen: Elemental analysis with external beam methods. Nuclear Instruments and Methods B40/41 (1989) p. 638
- /6/ E. Rauhala, J. Räisänen: Stopping powers of 0.5-8.3 MeV protons in Havar, Nickel, Kapton and Mylar. Nuclear Instruments and Methods B35 (1988) p. 130
- /7/ T. Tuurnala, A. Hautojärvi, K. Harva: Nondestructive analysis of paintings by PIXE and PIGE. Studies in Conservation 30 (1985) p. 93
- /8/ W. Rudolph, D. Grambole, R. Groetzschel, C. Heiser, F. Herrmann, P. Knothe, C. Neelmeijer: Hydrogen, oxygen and carbon losses during ^{15}N bombardment of PMMA layers. Nuclear Instruments and Methods B33 (1988) p. 803
- /9/ H.-P. Schramm, C. Neelmeijer, H. Matthes, W. Pfestorf: Möglichkeiten und Grenzen der zerstörungsfreien Pigmentanalyse auf Gemäldeoberflächen mittels externem Protonenstrahl. Wiener Berichte über Naturwissenschaften in der Kunst. Wien: VWGÖ, vol. 4/5 (1987/88) p. 26
- /10/ D.D. Cohen, M. Harrigan: K- and L-shell ionization cross sections for protons and helium ions calculated in the ECPSSR theory. Atomic Data and Nuclear Data Tables 33 (1985) p. 255
- /11/ A.Th. Haberditzl: Untersuchungen über Abbauprozesse an Pergament. Dissertation an der Technischen Universität Wien, 1987
- /12/ H.-P. Schramm, B. Hering: Historische Materialien und ihre Identifizierung. Berlin 1989, auch Graz 1989
- /13/ "Der Zwist um Dortmunds Caspar David Friedrich". Kölnische Rundschau, 22.10.1988;
"Winterlandschaft von Friedrich gemalt"; and
"Winterlandschaft echt - aber doch eine Zweitversion?". Ruhrnachrichten, 22.10.1988;
"Experte: Dortmunder 'Friedrich' echt". WR vom 22.10.1988
- /14/ T. Tuurnala, A. Hautojärvi, K. Harva: Examination of oil paintings by using a PIXE/PIGE combination. Nuclear Instruments and Methods B14 (1986) p. 70

ABSTRACT

This paper reports on the observations made on samples from five Italian paintings (13th/16th centuries) using Differential Scanning Calorimetry (DSC). Previous studies of paint samples using Differential Thermal Analysis (DTA) have demonstrated that the resulting curves are sensitive to the age of the sample¹, its chemical composition and the type of white pigment used². DSC provides a direct measure of the heat evolved during an exothermic reaction and so it can be used to quantify the effects previously observed using DTA.

KEYWORDS

Differential Scanning Calorimetry, Binding Media, 13th/16th century Italian Paintings.

A NOVEL APPROACH TO THE PROBLEM OF CHARACTERIZING THE BINDING MEDIA IN EARLY ITALIAN PAINTINGS (13th/16th CENTURY)

Marianne Odlyha
Birkbeck College
University of London
29 Gordon Square
London WC1H 0PP
U.K.

Courtauld Institute of Art
Somerset House
Strand
London WC2R 0RN
U.K.

INTRODUCTION

Outline of the approach to the problem

The basic problem in characterizing binding media lies in the small amount of sample which is available and that the sample is often a complicated mixture of materials which have aged or changed in the process of various restoration treatments.³ Then there is the additional problem of suitable reference materials and the influence of pigment mixtures.

The aim of this paper is to demonstrate that with careful sampling and small sample size it is possible to obtain DSC curves which reflect the type of medium used. Furthermore, measurement of the accompanying DSC parameters allows for quantification of the observed phenomena.

The starting point of the investigation focussed on samples from a painting attributed to Coppo di Marcovaldo from the Chiesa del Carmine in Florence. As this is a painting from the second half of the 13th century it represents an example of an early tempera painting. Microchemical tests also confirmed the presence of proteinaceous medium.⁴ Hence the DSC curves obtained from samples taken from this painting could be considered to represent standard curves for old proteinaceous material. These curves were then used to interpret results from the following paintings:

Tintoretto: The assumption of the Virgin Mary (*ca.* 1560),
Bamberg Cathedral.
L'Ortonlano: Museo di san Martino Naples (1521).
Giovanni Bellini: The death of St. Peter Martyr.
Francesco Giorgio di Martini: Nativity of Christ. (*ca.* 1500)

It is anticipated that the resulting DSC curves and measured parameters will assist in characterizing future samples from paintings of this period. A comparison of the data obtained was also made with those resulting from standard samples containing lead white/egg yolk and lead white/egg yolk and oil mixtures which had been prepared in the laboratories at the Fortezza da Basso in Florence in 1978.

Outline of Method

Differential scanning calorimetry (DSC) measures the heat flow to or from a sample as it is heated against a reference material at a selected rate. In the absence of sample the two holders (sample and reference) are balanced and give rise to a steady baseline over the required temperature range. In the presence of sample the imbalance due to heat flow to or from the sample gives rise to a peak where the parameters of onset temperature (T_0), peak area (A) and peak height (H) are measured.

Experimental

(a) Sampling: Samples were taken from the upper layers of the paintings from areas where the varnish had been previously removed either mechanically or by cleaning with a solvent. A small amount was taken by scraping the surface with a scalpel blade and transferring the material to a glass slide.

(b) DSC Measurements: Samples (0.1 – 0.4 mg) were heated in platinum crucibles in oxygen (flow rate 60 cm³/min). The heating was carried out in a Perkin-Elmer DSC-7, and the parameters were evaluated using the TAS-7 software.

Results and Discussion

The white sample from the 13th century painting attributed to Coppo di Marcovaldo gave rise to a DSC curve as shown in Fig. 1a. The peaks represent the oxidation of the organic component together with the change of lead white pigment to red Pb_3O_4 and finally, if heated to 650°C , to yellow PbO .

The similarity of the two curves (Figure 1a/b) indicates that the samples have similar chemical composition. If the curve from the Coppo di Marcovaldo sample (Figure 1a) is considered as being representative of an early tempera painting then the sample from the Martini painting (Figure 1b) must also be of that type. In both cases the dominant exothermic peak occurs over the temperature range 170°C to 350°C with a peak maximum in the region of $270\text{--}280^\circ\text{C}$.

Fig. 1

- 1(a) Coppo di Marcovaldo
1(b) F di Giorgio Martini

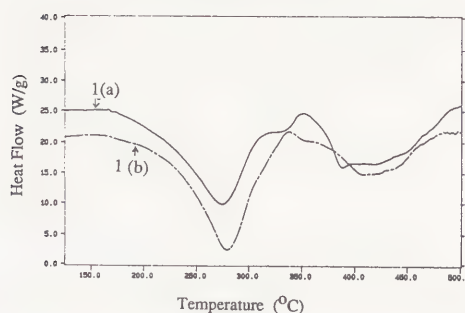
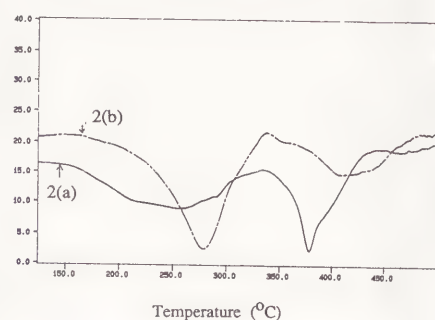


Fig. 2

- 2(a) F. di Giorgio Martini
2(b) F. di Giorgio Martini



The Martini sample was taken from the white of the architectural background. Another white sample from the same painting taken from the dog's paw in the foreground gave rise to quite a different DSC curve, Figure 2a. Here the dominant exothermic peak appears in the temperature range $350\text{--}450^\circ\text{C}$ with a peak maximum in the region of 370°C . There is another peak in the region 160 to 350°C but this is broader and considerably smaller than the main exothermic peak of the first Martini sample, Figures 1b & 2b. From previous work⁵ this curve is identifiable as that which is obtained from an oil-based medium.

Figure 3a shows the DSC curve of a white sample from the Bellini painting (white area of shield). This is similar to the Martini sample (Figure 2a/3b), in oil-based medium, except that both peaks have been shifted to higher temperatures. GC/MS work⁶ has indicated that the medium contains a drying oil which has been heat-bodied. The latter may well introduce a greater degree of cross-linking in the oil and this would result in the oxidative degradation processes occurring at higher temperatures. Further samples need to be studied to confirm this observation.

Fig. 3

- 3(a) Giovanni Bellini (shield)
3(b) F di Martini (dog's paw)

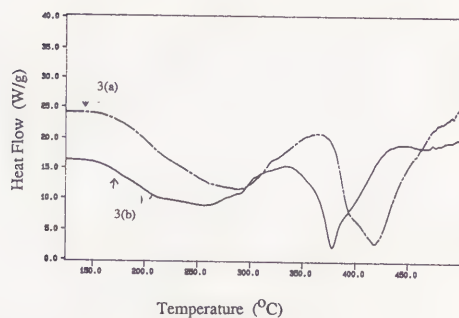
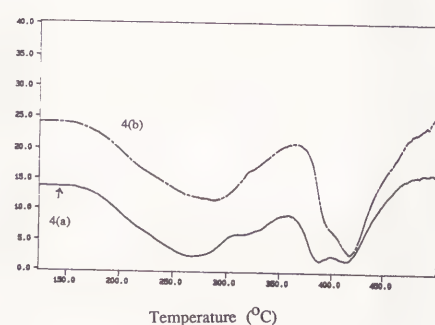


Fig. 4

- 4(a) Giovanni Bellini (robe)
4(b) Giovanni Bellini (shield)



A sample from a different area in the Bellini painting, the white of the Dominican robe, gave rise to a DSC curve (Figure 4a) where the total exothermic effect is less than the value for the previous sample (heat-bodied oil) but greater than that obtained for the egg tempera sample (Figure 1a).

In the case of standard samples (Figs. 5 & 6) prepared in 1978 the total measured exothermic effect was found to be greater for linseed oil/lead white than for a mixture of linseed oil/egg yolk/lead white, and this in turn was greater than that measured in a sample of egg yolk/lead white. (Table 1). Hence it appears likely that the sample from the white of the Dominican robe contains a mixture of oil and egg tempera (fig 7).

Fig. 5 Standards

- 5(a) Linseed oil/Egg yolk
5(b) Linseed oil

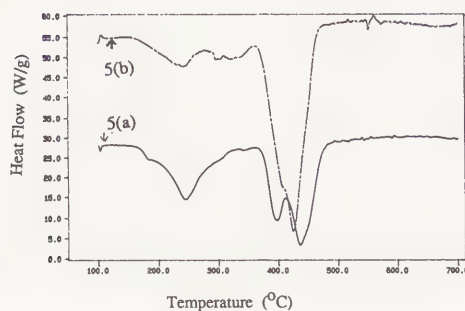


Fig. 6 Standards

- 6(a) Linseed oil
6(b) Egg yolk

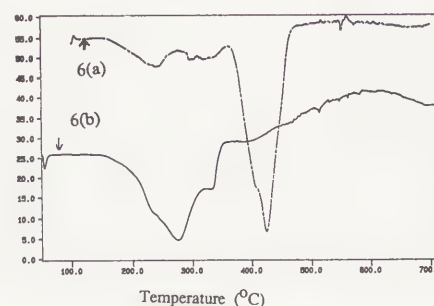


Table 1

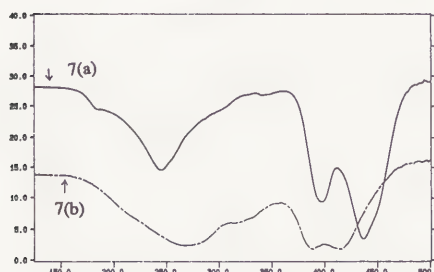
Measured Enthalpy Value (ΔH) for Total Observed Exothermic Effect.

Figure no.	ΔH	Medium Type
3a	4498.6	heat-bodied oil
4a	3705.9	oil/egg tempera
1a	3193.2	egg tempera
6a/5b	5709.4	linseed oil
5a	3986.1	linseed oil/egg yolk
6b	3383.0	egg yolk

$\Delta H = Jg^{-1}$

Fig. 7

- 7(a) Linseed oil/Egg yolk (standard)
7(b) Giovanni Bellini (robe)



GC/MS measurements confirmed that the medium contained a drying oil with some egg tempera.

Figures 8 and 9 show additional results obtained from samples taken from green areas from four of the paintings. The DSC curves in Figure 8 are similar to the tempera-type of Figure 1. The stronger exothermic nature of the first peak can be attributed to pigment interaction which would occur to a larger extent with Cu based pigments and proteinaceous medium than with lead white. The green sample from the Tintoretto painting was analysed by emission spectroscopy and was found to contain Cu-type pigments.⁷ Microchemical tests also indicated the presence of protein. Figure 9 shows curves which are similar to Figures 3a and b, oil-type.

Fig. 8

8(a) Tintoretto
8(b) Coppo di Marcovaldo

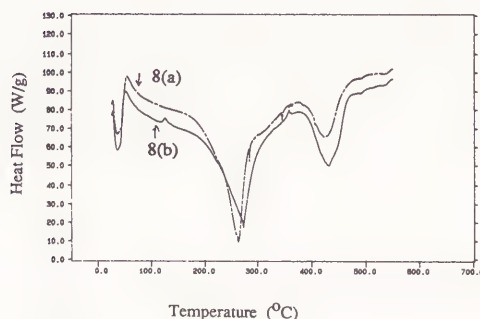


Fig. 9

9(a) Giovanni Bellini
9(b) L'Ortonlano

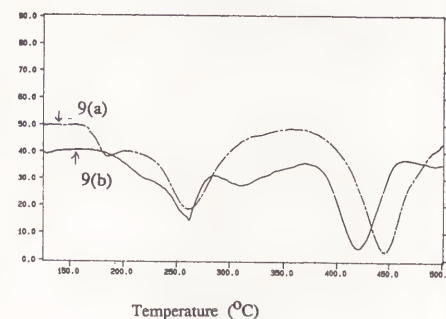


Table 2

DSC Parameters for White Samples.

Figure No.	1 st Exotherm			2 nd Exotherm		
	T _{0,1}	H ₁	A ₁	T _{0,2}	H ₂	A ₂
1a	171.8	14.9	1650	366.0	9.0	1173
1b	174.3	19.1	1854	367.0	6.9	775
2a	163.5	6.8	1068	360.6	14.8	848
3a	176.4	10.4	1709	378.3	18.8	1523
4a	175.9	8.9	1345	368.3	10.5	963
5a	167.7	12.9	1317	375.2	24.9	2289

Note: T₀ = °C; H = Wg⁻¹; A = Wg⁻¹.min

Table 3

DSC Parameters for Green Samples.

Figure No.	1 st Exotherm			2 nd Exotherm		
	T _{0,1}	H ₁	A ₁	T _{0,2}	H ₂	A ₂
8a*	261.7	70.5	5947	386.2	24.2	1660
8b*	193.9	56.3	5272	395.4	33.9	2346
9a*	187.3	24.1	2386	387.8	32.3	1939
9b	168.8	30.5	3332	399.7	44.8	3677

* Samples were heated in aluminium crucibles.

GC/MS confirmed that the medium of the sample from the green of the plants in the Bellini painting does contain a heat-bodied oil. This again could be the reason for the noticeable shift of the high temperature exotherm of the Bellini sample to higher temperatures. The calculated DSC parameters for the white samples are given in Table 2; those for the green samples are given in Table 3.

Conclusions

DSC curves and calculated parameters indicate that it is possible to quantify the observed differences and then to use such information for pattern recognition of future samples. The small sample size and no sample pre-treatment offers an attractive method which together with GC/MS or pyrolysis/MS should provide a powerful means for characterizing binding media.

References

1. Preuser, F. Thermal Anal. 161, 979, 272-283.
2. Odlyha, M. and Burmester, A. Thermal Anal. 3, 1988, 1041-1052.
3. Reichlin-Minoretti, A. Bindemittelanaysen an Vorindustriellen Malereien. Diss ETH No. 7377 p.34 Zurich 1983.
4. Ibid. p.44
5. See ref. 2, page 1051.
6. Private communication Raymond White, Scientific Dept., National Gallery, London.
7. Die Bamberger "Himmelfahrt Mariae" von Jacopo Tintoretto. Internationale Kolloquium in München. 27-28th Januar 1986 und Restaurierungsbericht Arbeitsheft, 42-Bayerisches Landesamt für Denkmalpflege, p.135.

ABSTRACT.

Wax seals and dyed textile attachments from parchment documents from the XIII to the XVIII century were analyzed by I.R. spectroscopy, U.V. spectroscopy, X-ray fluorescence and thin layer chromatography. Preliminary results on the variation of materials used for manufacture are given.

KEYWORDS

Wax-seal, attachment, beeswax, colophony, dyestuff, I.R. spectroscopy, U.V. spectroscopy, X-ray fluorescence, thin layer chromatography.

CHEMICAL ANALYSIS OF WAX SEALS AND DYED TEXTILE ATTACHMENTS FROM PARCHMENT DOCUMENTS. PRELIMINARY INVESTIGATIONS.

Enrique Parra* and Andrés Serrano
I.C.R.B.C.
C/. Greco, 4. Madrid 28040.
Spain.

Introduction.

Spain is very rich in sigillographic holdings, forgotten until only a few years ago. Only a small quantity of seals are restored and in many cases an empirical recipe was followed, without taking into account the internationally accepted restoration criteria. Very few seals have been treated in specialized centers as a result of a lack of technical and personal resources.

In 1988, the Spanish Culture Ministry decided to initialize a comprehensive project to conserve all sigillographic collections and the laboratories and workshops of the Instituto de Conservación y Restauración de Bienes Culturales were charged with this responsibility. This project was divided in different sections according to original archives of the collections. Its objectives were the study, restoration and conservation of the seals and the attached parchment documents.

Our institution was able to study a large number of wax seals originating from different Spanish Archives, the collections include royal, ecclesiastical, council and private seals, as well as those from royal houses abroad.

The initial aim of the present study was to determine the components of wax seals and its textile attachments and to use this information to deepen the understanding of the materials used by the craftsmen in different periods. Another important intention of the study was to obtain more data about textile dyestuffs employed in Spain and its variation during Spanish history.

Description of the materials analyzed.

Wax seals and dyed textile attachments belonging to the State Archives were analyzed. The Archives represented in the collections are:

- Archivo Histórico Nacional, Madrid (royal, council and private seals).
- Archivo General de Simancas, Valladolid (royal seals).
- Archivo de la Corona de Aragón, Barcelona (royal seals).
- Archivo Histórico Provincial de Mallorca, Mallorca (royal seals).
- Archivo Histórico Provincial de Teruel, Teruel (royal and council seals).

This study of royal seals from these archives investigated the amount of variety in raw component materials and the evolution of the materials used during the period investigated.

The textile attachments of the seals are a previously uninvestigated source of textile fibres and dyestuffs. As these materials are inclusions in the wax or other organic material imbedded in the seal body, it is possible to obtain a large enough sample to achieve a complete research study of textile dyestuffs in very well documented and dated pieces of the period XII to XX century.

During the initial phase of the research project, we analyzed almost 80 samples of wax and wax resin mixtures, and nearly 130 samples of dyed textile fibres belonging to 70 wax seals. This is only a small part of the large number of seals (approximately 600) available for study.

Experimental conditions

Wax analysis was performed by means of I.R. spectroscopy using a melted film of the sample between NaCl windows, in a Perkin Elmer 257 apparatus (4000 to 600 cm⁻¹). Wax-resin mixtures were first examined by I.R. spectrometry, and the presence of resin and its type was confirmed by thin layer chromatography. The conditions used were: thin layer aluminium plates coated with silica gel 60F254 (Merck) eluted with chloroform : ethyl acetate (3 : 1), and developed with U.V. light (350 nm.) and/or a 5% solution of antimony pentachloride in carbon tetrachloride. We used as standards beeswax, ceresin, carnauba wax, colophony, dammar, sandarac and mastic resins.

The presence of colophony resin was also confirmed in every case by its U.V. spectrum in ethyl alcohol, using a Perkin Elmer Hitachi 200 spectrophotometer. The treatment of the sample was as follows: after diluting 0.5 mg sample in 1 ml. of ethyl alcohol, the resulting mixture was stirred over -

night and filtered; then the spectrum was recorded. Abietic and neoabietic acids, if present, strongly absorb at 243-245 nm. (1).

Elemental analysis of pigments in red seals was determined by X-ray fluorescence spectrometry using a Kevex XRF 0700 apparatus.

Dyestuffs in textile attachments were analyzed by thin layer chromatography under previously published conditions(2).

Results and Discussion

In every case, the analysis of wax seals (red or uncoloured) revealed that the only materials used were beeswax, or beeswax - resin mixtures, in the latter only colophony could be found.

Red seals were all coloured with cinnabar; this was deduced from the fact that mercury was the only metal detected by X-ray fluorescence. These results are shown in Table 1, in which we detail the qualitative composition of some of the samples analyzed within the limits of detection of the techniques employed.

The ratios of wax/resin, wax/cinnabar or wax/resin/cinnabar could not be quantified using this technique for several reasons. Cinnabar (HgS) does not absorb in the I.R. zone studied and wax/resin mixtures cannot be quantified by I.R. or U.V. analysis because of changes in the original composition due to ageing processes in terpenic resins (3). Further study is now underway using gas liquid chromatography to determine the proportion of wax/resin.

Some conclusions can be drawn from the data in Table 1. For instance, there is not a great variation in the materials used for manufacture of seals. Most of the pieces, dated between the XII and XV centuries are made exclusively of beeswax (uncoloured or brown seals) or beeswax-cinnabar mixtures (red seals).

Another important fact is that colophony seems to appear first during the reign of Alfonso IV Rey de Aragón (1327-1338). Previously no seal seems to have resin in its composition. Later Alfonso V (1457) and Felipe V (1700 - 1746) included resin -colophony- in the composition of their personal seals. Seal no. 9578, belonging to Carlos II Rey de Sicilia (1285 - 1309) is the only exception; the inclusion of colophony may relate to the fact that it comes from outside Spain.

So we have discovered that the royal seals from the XIV century to the present have resin in their composition. This finding differs from the English seals' composition studied by D. Robins *et al.*(4) by the 13-C Nuclear Magnetic Resonance technique. They found that all the medieval English royal seals studied are composed only of beeswax.

We cannot conclude with absolute certainty that before 1327 any seal does not contain resin in its composition. There are still a lot of pieces to analyze and we have also to remark the possibility that very small quantities of resins (for example, used for giving more plasticity to wax) could be out of the limits of detection of our techniques. This is another reason to study this mixtures by G.L.C.

A curious seal is no. 9568 which belongs to Pedro III, which differs from the rest of the seals because it is made of a paraffin wax, probably ceresin.

The dyestuff analysis of the textile attachments reveals new data on the exhaustively studied world of natural textile dyestuffs (4). These data are shown in Table 2. Some attachments could not be analyzed because it was impossible to obtain samples.

As we can see from Table 2, weld is the only dyestuff employed for dyeing yellow, and its stability over the time and light-fastness is very good. Weld is also used for greens (with indigo) and for brown (no. 9574). Quercitron is only found in one sample (no. 9565) which belongs to a seal coming from outside Spain.

In dyeing red, madder is preferred in most cases, substituted by kermes only in two samples (no. 9496 and no.9526), all before the XVI century. Cochineal carminic acid is found also in two samples dated in the XVIII century (no. 9528 and 9529).

Blue colours are always dyed with indigo, as usual and only mixed on certain occasions with weld and madder (see Table 2) to obtain different shades, or possibly, due to manufacturing constraints.

All these results are in agreement with those previously reported by other authors (5).

Two curious samples are no. 9543 and 9575, in which we find lac as

red dyestuff. It should be interesting to see how this dyestuff arrived to Spain in that ancient time (these samples belong to attachments from seals of the XIV and XV centuries). Nevertheless, there is always the possibility that its presence in these attachments could be due to restoration work done in the XVIII or XIX century. This point has still not been investigated.

Conclusions

As a part of a global study of wax seals made from the Middle Ages to the XVIII century, we have seen only a little variation in the composition of organic materials employed. Every seal dated before the XIV century is only composed of beeswax. During the reign of Alfonso IV Rey de Aragón colophony seems to have been introduced.

We hope to find more variations in composition (including variations in quantitative composition) by studying more modern seals and introducing other techniques (such as G.L.C.) to obtain more accurate results.

The variation in the dyestuff composition is in agreement with the dyeing methods employed in Europe and described by many authors (5).

Acknowledgements.

Thanks to Miss M. Dolores Gayo for the X-ray fluorescence analysis. Thanks also to Docugraf S.C. for the samples provided, and to Miss Carmen Rueda for helpful discussion.

References

1. F.J. Ball and W.G. Wardell. "Determination of Rosin Acids in Tall Oil Using 240-250 nm. Absorption Characteristic of Abietic Type Acids." Journal of American Oil Chemist's Society, 28, (1951), 137-140.
2. J.H. Hofenk-deGraaf. "L'analyse des Matieres Colorantes dans les Textiles Anciens". Bulletin de la Liaison du C.I.E.T.A. no. 35, (1972), 12-20.
3. J.S. Mills and R. White. The Organic Chemistry of Museum Objects, (London, Butterworths, 1987), 87-90.
4. D. Robins, A. Alstin and D. Fletton. "The Examination of Organic Components in Historical Non-Metallic Seals with C-13 Fourier Transform Nuclear Magnetic Resonance Spectroscopy". ICOM Committee for Conservation, Sydney, 1987, 87-92.
5. See for example J.H. Hofenk-deGraaf. "Natural Dyestuffs. Origin Chemical Constitution and Identification". ICOM Committee for Conservation, Amsterdam, 1969.

no.	Colour	Beeswax	Colophony	Cinnabar	Cronology	Origin	Belongs to
9491	red	+	-	+	1390	A. Teruel	Juan I R. Aragón
9492	red	+	-	+	1436-1387	A. Teruel	Juan II R. Navarra
9495	red	+	-	+	1387-1395	A. Teruel	Jaime I R. Aragón
9496	brown	+	-	-	1213-1276	A. Teruel	Jaime I R. Aragón
9497	red	+	-	+	1344-1386	A. Teruel	Pedro IV R. Aragón
9498	brown	+	-	-	1250	A. Teruel	Jaime I R. Aragón
9499	brown	+	-	-	1267-1300	A. Teruel	Concejo de Teruel
9500	red	+	-	+	1387-1395	A. Teruel	Juan I R. Aragón
9501	red	+	-	+	1416-1458	A. Teruel	Alfonso V R. Aragón
9503	red	+	-	+	1336-1387	A. Teruel	Pedro IV R. Aragón
9505	red	+	-	+	1388	A. Teruel	Violante de Bar
9507	red	+	-	+	1327-1336	A. Teruel	Alfonso IV R. Aragón
9509	brown	+	-	-	1343-1349	Mallorca	Jaime III R. Mallorca
9510	red	+	-	+	1336-1387	Mallorca	Pedro IV R. Aragón
9511	red	+	-	+	1336-1387	Mallorca	Pedro IV R. Aragón
9512	red	+	-	+	1336-1387	Mallorca	Pedro IV R. Aragón
9513	red	+	-	+	1336-1387	Mallorca	Pedro IV R. Aragón
9519	red	+	-	+	1387-1395	Mallorca	Juan I R. Aragón
9525	red	+	-	+	1395-1410	Mallorca	Martin I R. Aragón
9526	red	+	+	+	1416-1458	Mallorca	Alfonso V R. Aragón
9527	red	+	-	+	1416-1458	Mallorca	Alfonso V R. Aragón
9528	red	+	+	+	1700-1746	Mallorca	Felipe V R. España
9528'	red	+	+	+	1700-1746	Mallorca	Felipe V R. España
9530	red	+	-	+	1395-1410	Mallorca	Martin I R. Aragón
9542	red	+	-	+	1233	A. H. N.	Urraca López de Haro
9543	brown	+	-	-	1229	A. H. N.	Alfonso IX R. León
9544	brown	+	-	-	1181	A. H. N.	Alfonso VIII R. Cast.
9545	brown	+	-	-	1285	A. H. N.	Sancho IV R. Cast.-Le.
9546	brown	+	-	-	1285	A. H. N.	Sancho IV R. Cast.-Le.
9547	brown	+	-	-	1285	A. H. N.	Sancho IV R. Cast.-Le.
9548	brown	+	-	-	1316	A. H. N.	Alfonso IX R. Cast.-Le.
9549	brown	+	-	-	1346	A. H. N.	María de Portugal
9565	brown	+	-	-	1313	C. Aragón	Ciudad de Nueburgo
9562	red	+	-	+	1344	C. Aragón	Pedro III R. Aragón
9563	red	+	-	+	1430	C. Aragón	Alfonso V R. Aragón
9564	red	+	+	+	1457	C. Aragón	Alfonso V R. Aragón
9568	red	-**	-	+	1276-1285	C. Aragón	Pedro III R. Aragón
9569	red	+	-	+	1291-1327	C. Aragón	Jaime II R. Aragón
9570	red	+	+	+	1327-1336	C. Aragón	Alfonso IV R. Aragón
9571	red	+	+	+	1327-1336	C. Aragón	Alfonso IV R. Aragón
9572	red	+	+	+	1327-1336	C. Aragón	Alfonso IV R. Aragón
9575	red	+	-	+	1458-1479	C. Aragón	Juan II R. Aragón
9578	brown	+	+	+	1285-1304	C. Aragón	Carlos II R. Sicilia

Table 1.- Results of the analysis of some of the seals studied.

Key:

Mallorca= Archivo Histórico Provincial del Reino de Mallorca.

C. Aragón= Archivo de la Corona de Aragón.

A.H.N.= Archivo Histórico Nacional.

A. Teruel= Archivo Histórico Provincial de Teruel.

*= Only a small quantity was detected.

**=Ceresin.

Seal no. 9528 has two different parts. Both of them were analyzed.

no.	Fiber	Colour	Dyestuff	Chronology	Origin	Belongs to
9491	silk	red yellow	madder weld + madder	1390	A. Teruel	Juan I R. Aragón
9492	silk	red yellow	madder weld	1436	A. Teruel	Juan II R. de Navarra
9405	silk	red yellow	madder weld	1387-1395	A. Teruel	Juan I R. Aragón
9496	silk	red yellow	kermes + madder weld	1213-1276	A. Teruel	Jaime I R. Aragón
9497	silk	red yellow	madder weld	1344-1386	A. Teruel	Pedro IV R. Aragón
9498	silk	yellow	weld	1250	A. Teruel	Jaime I R. Aragón
9499	silk	yellow	weld	1267-1300	A. Teruel	Concejo de Teruel
9500	silk	yellow red	weld + madder madder	1387-1395	A. Teruel	Juan I R. Aragón
9501	silk	yellow red	weld madder	1416-1458	A. Teruel	Alfonso V R. Aragón
9503	silk	yellow red	weld madder	1387-1395	A. Teruel	Pedro IV R. Aragón
9505	silk	yellow red	weld madder	1387-1388	A. Teruel	Violante de Bar
9507	silk	yellow red	weld madder	1327-1336	A. Teruel	Alfonso IV R. Aragón
9509	silk	yellow red	weld madder	1340-1349	Mallorca	Jaime III R. Mallorca
9512	silk	yellow red	weld madder+indigo	1336-1387	Mallorca	Pedro IV R. Aragón
9513	silk	yellow red	weld madder	1336-1387	Mallorca	Pedro IV R. Aragón
9525	silk	yellow red	weld madder	1395-1410	Mallorca	Martín I R. Aragón
9526	silk	yellow red	weld kermes	1416-1458	Mallorca	Alfonso V R. Aragón
9527	silk	yellow red	weld madder	1416-1458	Mallorca	Alfonso V R. Aragón
9528	silk	yellow red	weld cochineal	1700-1746	Mallorca	Felipe V R. España
9529	silk	yellow red	weld cochineal	1700-1746	Mallorca	Felipe V R. España
9530	silk	yellow red	weld madder	1395-1410	Mallorca	Martín I R. Aragón
9542	silk	yellow red	weld madder	1233	A. H. N.	Urraca López de Haro
9543	silk	yellow orange	weld weld+lac dye	1299	A. H. N.	Alfonso IX R. León
9545	silk	yellow red white	weld madder	1285	A. H. N.	Sancho IV R. Castilla y León
9546	silk	yellow red blue	weld weld+madder weld+indigo	1285	A. H. N.	Sancho IV R. Castilla y León
9547	silk	blue brown white	weld+indigo weld	1285	A. H. N.	Sancho IV R. Castilla y León
9548	silk	yellow red	weld madder	1316	A. H. N.	Alfonso XI R. Castilla y León
9549	linen	yellow blue	weld weld+indigo	1346	A. H. N.	María de Portugal

Table 2.- Results of the dyestuffs analysis in the attachments of some of the seals studied.

Key:

A. Teruel: Archivo Histórico Provincial de Teruel

Mallorca : Archivo Histórico Provincial del Reino de Mallorca

A. H. N. : Archivo Histórico Nacional.

R. = King of

no.	Fiber	Colour	Dyestuff	Chronology	Origin	Belongs to
9551	silk	yellow red	weld madder	1379	A. H. N.	Leonor de Aragón
9562	silk	yellow red	weld madder+gallic a.	1344	C. Aragón	Pedro III R. Aragón
9563	silk	yellow red	weld madder+gallic a.	1430	C. Aragón	Alfonso V R. Aragón
9564	silk	yellow red	weld kermes	1457	C. Aragón	Alfonso V R. Aragón
9565	silk	yellow	quercetin	1313	C. Aragón	Ciudad de Nueburgo
9568	silk	red	madder+gallic a.	1344	C. Aragón	Pedro III R. Aragón
9570	silk	yellow red	weld madder+gallic a.	1327-1336	C. Aragón	Alfonso IV R. Aragón
9571	silk	yellow red	weld madder+gallic a.	1327-1336	C. Aragón	Alfonso IV R. Aragón
9575	silk	yellow red	weld lac dye	1458-1479	C. Aragón	Juan II R. Aragón
9578	silk	yellow blue	weld indigo+weld	1285-1304	C. Aragón	Carlos II R. Sicilia

Table 2. (Cont.).- Results of the dyestuff analysis in the attachments of some of the seals studied.

Key:

A. H. N.: Archivo Histórico Nacional

C. Aragón: Archivo de la Corona de Aragón

R. = king of

gallic a. = gallic acid

ABSTRACT

The paper presents the results of comparative analysis of West-European and Russian technology of production formulas for blue and green copper compounds used as pigments in painting; it generalizes methods of producing copper pigments, described in Russian 17-18th century manuscripts.

In spite of the fact that Russians knew West-European medieval instructions on the production technology of painting materials, most of Russian formulas suggest a different method of obtaining copper salts. The principal difference is the use, of milk and other products such as cheese, curd and yeast in read of vinegar.

This paper publishes for the first time original texts drawn from authentic icon painting works and books of technological formulas.

KEYWORDS

Recipe manuscripts, copper pigments, verdigris, of Russian pigment technology recreation.

RUSSIAN 17-18TH CENTURIES PRODUCTION FORMULAS FOR BLUE AND GREEN COPPER PIGMENTS

S.A. Pisareva, Yu.I. Grenberg
10 Krestyanskaya Pl., Moscow
VNIIR
U.S.S.R.

Introduction

The history of using copper salts as pigments takes its beginning in antiquity. The ease with which copper interacts with different substances, its capacity to form chemical combinations of blue - green gamut of colour with various shades and the possibility of using them as pigments were the reason for searching the various ways of their production.

Ancient technological recipes

A most complete description of various copper products is given by Pliny (XXXIV, 26) /1/, who names them 'aerugo' (lat. 'aeris robigo' means copper rust). According to Pliny, 'aerugo' includes various blue-green corrosion products formed both naturally on the surface of copper ores, metallic copper and its alloys, and by the action of vinegar. But these is, Pliny points out, another kind of 'aerugo', that he calls 'scolex', obtained by grinding alum, salt and soda along with strong vinegar in a copper mortar.

One and the same combination, acetic copper, is described by both Theophrastus (357) /2/ and Vitruvius (XII, 7) /3/. In so doing, Theophrastus calls this product in Greek 'ios xarkov', i.e. copper rust, like Pliny 'aerugo' and Vitruvius 'aeruca' in Latin. Alongside that, although Pliny used the term similar to Vitruvius, he describes methods of producing copper salts, belonging to different categories of chemical combinations.

For a long time there was a confusion among writers, caused, perhaps, by translation of ancient names of copper pigments. All green copper pigments, produced artificially, were, as a rule, termed 'verdigris' (Engl.), 'Grünspan' (Germ.), 'vert-de-gris' (Fr.), 'verderame' (Ital.) and 'yar-medyanika' (Rus.). Again, in Theophilus treatise green copper pigments, produced in different ways and given different names (De viridi salso, De viridi Hispanico), have also different chemical composition, which was experimentally confirmed by Kühn /4/. This was also confirmed by subsequent investigations of green copper pigments when studying works of painting /5/.

By observing the development of production technology of copper pigments, one can easily see that formulas, included in many West-European medieval books, are based virtually on the methods described by Pliny.

Thus, Pliny was the first to describe the method of producing copper salts on copper plates suspended over strong vinegar in tightly closed vessels. In the Middle Ages this technique was developed further, when different reagents, vinegar, sal-ammoniac, urine and others, acted on copper plates lubricated with honey and salt beforehand.

Pliny wrote also of white copper, i.e. copper and silver alloy, being used for the same purpose. We also find indication that silver was used to produce blue pigments in medieval treatises.

The antique tradition of making copper pigments not only does not disappear with the end of the Middle Ages, but is put in the basis of further experiments in this direction (see, e.g., de Mayern's 17th century manuscript).

Of particular interest in this respect is an old Russian technological tradition. In numerous Russian manuscripts (icon painting originals and collected works of different content) there are many production formulas for making copper pigments which were termed in Russia 'copper yar' or 'yar-medyanika' (verdigris), possibly derived from the Greek 'yar'. (In 'Erminia' by Dionysius a similar pigment was called 'vardaramon' or 'tsingary - τσίγγαρι').

A written technological tradition was formulated in Russia not earlier than mid-17th century. Judging by manuscripts that were preserved, the formula for producing pigments under considera-

tion was laid down only early in the 17th century. Methods of producing artificial blue-green pigments were, however, known without doubt long before this time. Russian masters knew quite well West-European formulas for producing copper pigments and white lead by acting on copper and lead plates with vinegar, which is proved by formulas that reached us: translated from Latin.

Along with that, the bulk of Russian technological formulas suggest a different way of producing copper salts suitable for use as pigments. The principal difference between Russian and West-European formulas is the absence in them of a recommendation to use vinegar. The reason for this is, probably, that in Russia there was no cheap vinegar which South- and West-European masters had in abundance.

Vinegar was first mentioned in Russian written documents in mid-15th century /11/; in the 16th century it was served as condiment at the Czar's repasts and was known as Rhein vinegar, i.e. was imported. It is quite possible that already at that time Rhein vinegar was sometimes replaced by domestic product made of honey, which is indicated by the term 'acid honey vinegar' used at the time. This does not give reason to believe, however, that this product was in any way commonly used. Russian formulation proper for producing copper pigments did not embody it either.

Thus, having no vinegar in sufficient quantity, but familiar with the action of weak organic acids on copper, Russian masters used them in the form of dairy and sour milk products: milk, curd and cheese, and also yeast.

Russian technological recipes

Setting aside formulas borrowed by Russian compilers of technological instructions direct from Latin sources, we studied about 70 Russian orders on preparing the so-called 'yar-med'yanka' (verdigris), which came down to us in early 17th - late 17th century copies. All these guiding documents can be classified, on the basis of compositions used to produce copper pigments, into several basic groups.

A number of formulas, the earliest of which reached us in a copy made in the second quarter of the 17th century, prescribes action on copper by honey, salt and cheese. This demonstrates Russian masters' familiarity with Western formulas laid down in Theophilus' treatise, describing the production of green pigment by acting on copper with honey and salt. Instead of vinegar, however, indicated in Theophilus' treatise, the Russian source recommends goat cheese. "If you desire to make verdigris, take fresh goat cheese from where it is made, salt and honey in quantities equal to a quarter of the cheese. Put all this in a copper vessel, cover it with a copper lid and place it in manure in the sun for two or three weeks. And verdigris would result"¹.

Russian masters also knew the technique of producing green copper pigments using blue vitriol, which may also be linked to the awareness of the medieval tradition. (We found the instruction to use Roman, i.e. blue vitriol, for the same purpose in section 81 of Jean le Begue's manuscript /12/). On the whole, however, we are dealing with the original Russian formula: "Take a copper pot, a quarter of cheese, a bezmen² of fresh milk, a zolotnik³ of blue vitriol. And put all this into the pot, cover it with a copper lid, cement it with dough and place it on the stove for two weeks. Put also pieces of copper into the pot" (second quarter of the 17th century).

Many formulas for making verdigris are based on the recommendation to use the interaction of copper with sour milk. The simplest formula which reached us in a copy made in the third quarter of the 18th century reads: "Take a copper kettle and lubricate it with sour milk. And do not touch it for three weeks or so. And verdigris would result".

In other cases sour milk is recommended to be used in a combina-

¹Translation into English was made from texts first translated into modern Russian.

²Bezmen is an old Russian measure of weight now obsolete. In the 16th century ledger bezmen was defined as equal to 240 zolotniks.

³Zolotnik is an old Russian measure of weight now obsolete. It is equal to 4.25 grams.

tion with other components, for instance, with cheese, as one of the manuscripts of the third quarter of the 17th century informs: "On verdigris. Place a copper vessel and pour sour milk into it and put in sour cheese crumbs (possibly, one must understand it as curd). And wet them with sour milk. And verdigris would result".

A set of articles, one of whose copies dates to the late 17th century, indicates the use, apart from the above - mentioned reagents, of cream of tartar; it is true though that the original text was greatly distorted by subsequent copyists: "Order for making verdigris. Take sour milk, curd, put them in a copper vessel and cover it with copper. Put right away copper fragments and copper scale in it. Put right away vine leaves or green grass in it. And keep it so for a month. And look in four times within a month mixing so as to keep it green". Recommendation to use vine leaves (or vein, as in other copies) is certainly a copyist's error. This paragraph in the formula meant no doubt cream of tartar. Recommendation of grass is, perhaps, an attempt to explain somehow an unintelligible indication of vine leaves. (Let us recollect, however, that addition of green grass was recommended in some West-European treatises to reinforce the colour of green copper salts).

We quoted several typical Russian formulas. All their variety comes to the following basic combinations of principal reagents acting on metal copper:

1. Yeast and honey.
2. Sour milk.
3. Sour milk and cheese.
4. Sour milk and cheese in the presence of white lead.
5. Sour milk, curd and cream of tartar.
6. Curd and raisin branches (possibly, grapevine is meant).
7. Fresh milk and cheese in the presence of blue vitriol.
8. Cheese, salt and honey.
9. Sal-ammoniac.
10. Soaked peas.

The above list of reagents shows that prevalent among them, as we have already noted, were milk and sour milk products.

From a chemical viewpoint fermentation of milk is a complex process during which not only lactic acid, but also other acids (acetic, propanoic and butyric oil acids), as well as carbonic acid, are formed (13/). Comparing individual old Russian orders to West-European formulas of Copper pigments, some Russian researchers expressed an opinion according to which all West-European practice of their making amounted to producing acetic copper, where as the use of dairy products aided Russian masters in making lactic copper with a substantial admixture of casein in it, which made the resulting pigments much duller. These conclusions were based on theoretical propositions alone, not substantiated experimentally.

Experimental Approach

In this connection we have begun an experimental work with a view identifying the composition of end products obtained in conformity with the formulas studied. To begin with, we reproduced the simplest of the existing formulas. A small piece of copper was covered with sour milk and placed in a warm spot. Two months later a green amorphous product was formed on the surface of copper. Two months later it was studied X-ray an diffraction in a by Debye-Sherrer camera, that proved to be an amorphous. Compound the infrared spectrum of this substance reveals adsorption bands belonging to acetate groups: 3400, 1580, 1430, 1170, 1030, 685 cm^{-1} . The experimental work on the investigation of old Russian formulas and comparison of the resulting data to the data, obtained by studying copper pigments taken from painting works, is going on. We hope to report on its results later on.

In conclusion we shall observe that methods of producing verdigris were as numerous as ways of grinding it to be used as paint. It was ground with alum, with onion juice, with vinegar and saffron, with saffron and rhubarb, with egg yolk, with drying oil, i.e. boiled linseed oil, and turpentine, with turpentine and vinegar, as well as with other substances.

Conclusions:

1. Pigment technologists are compared ancient, medieval European and Russian manuscripts.

2. Some Russian recepis are modeled. Some model pigment are indicated with IR-spectroscopi.

Bibliography

1. Questions of Technique in Naturalis Histori by Pliny the Elder. Bulletin of Ancient History. Supplement, 1946.
2. Theophrastus. On Stones. A modern Edition with Greek Text, Translation, Introduction and Commentary. Ed. E.R.Caley, F.F.Richards, Columbus, 1956.
3. Vetruius. Ten Books on Architecture. Moscow. The National Academy of Architecture, 1936, p. 149.
4. H.Kühn. Verdigris and Copper Resinate, St. in Conservation, 15(1970), 12-36.
5. E.H.van't Hul-Ehrnreich, P.B.Hallebeek. A new kind of old green copper pigments found, ICOM, 111rd Meeting, Madrid, october, 1972.
6. Theophil. Notes on Various Arts. Book 1, chapter 42. Report at the VTzNILKR (All-Union Central Research Laboratory of Conservation and Restoration), volume 7, Moscow, 1962.
7. Iraklion's Manuscript on Roman Arts and Paints, YIII-IX Centuries. Book 3, chapter 38. Report at the VTzNILKR, volume 4, Moscow, 1961.
8. Mappae clavicula. - Archeologia, v. 32, 1847.
9. Quoted from: E.Berger. History of Oil Paintine Technique Development, Moscow, 1961.
10. Russian reciepis are from manuscripts and are not publish.
11. V.A.Shchavinsky. Essay on the History of Painting Technique and Paint Technology of Ancient Russia. Moscow-Leningrad, OGIZ, 1935, pp. 103-104.
12. M.-P.Merrifield. Original treatises, dating from the XIIth to XVIIIth centuries...., v. 1, London, 1967.
13. J.G.Davis. Reference Dictionary of Dairy Farmong. Moscow, 1961.

ABSTRACT

Materials and technique of three Cima's paintings were studied. Stratigraphic analyses were carried out and the chemical nature of pigments was determined by SEM+EDS analyses.

The results obtained are discussed and compared with those concerning other paintings by Cima and other Italian painters of the period, as well as with instructions and recipes provided by antique treatises.

KEYWORDS

Cima, Painting-technique, Panel, 14th-15th century, Stratigraphy, EDS analyses, Paint recipes.

PAINTING TECHNIQUE OF CIMA DA CONEGLIANO AND ANALYTICAL-DOCUMENTARY COMMENTS ABOUT PIGMENTS

Raffaella Rossi-Manaresi and Antonella Tucci
Fondazione Cesare Gnudi - Centro di ricerca
Via Belle Arti, 56
40126 Bologna,
Italy

1. Introduction

The cleaning and restoration of three paintings by Cima da Conegliano was recently carried out in Bologna by Ottorino Nonfarmale. Our laboratory was commissioned to examine a number of samples taken before treatment. This was a welcome opportunity to study the paint structure and the more technical aspects of the artist's technique.

The works studied were the Sacred Conversation, dated about 1490, and S. Peter in the Chair dated 1516, both in the Brera Gallery, Milan; the Lamentation on the Dead Christ in the Pinacoteca Nazionale, Modena, which is probably from the artist's early period just as is the Sacred Conversation.

The study involved examination of paint cross-sections in incident and fluorescence light; identification of media by staining tests; identification of pigments by microchemical tests on unmounted samples and by determinations of elemental composition carried out on the sample cross-sections, using an X-ray energy dispersive spectrograph (EDS) connected to a scanning electron microscope (SEM).

The determination of the elemental composition of all layers in each sample allowed some considerations on the chemical nature of the pigments and comparison with information given by antique treatises and manuscripts which will be cited later when discussing the analytical results.

2. The ground

The three paintings showed a gesso ground. However, only the ground of the Lamentation, still on panel, is surely the original ground. In the past, the other two paintings were transferred from wood to canvas. Documentary information on the Sacred Conversation states clearly that the original ground, preserved during transfer, was removed in a subsequent intervention (1860) and substituted with a new gesso ground. The documents concerning the transfer of S. Peter in the Chair, carried out in 1883, do not provide technical information and we cannot know for sure if the original ground was preserved (1).

The gesso ground of the Lamentation, certainly original, appears rather homogeneous, possibly applied in two layers as suggested by a faint division between layers of gesso, detected in a sample including a relatively large amount of ground. The elemental analysis showed that in addition to calcium and sulphur, the gesso also contains traces of silica which may arise from the clay generally intercalated in the gypsum deposits (2).

The medium is animal glue, which gives a slight yellow stain to the white gesso. Staining of cross-sections for protein with amido black showed an increase of size content towards the top of the gesso layer, probably due to a final application of size intended to seal the ground (3). This is a practice clearly stated by Vasari's instructions "the gesso laid on the panel is smoothed and four or five coats of the smoothest size are spread over it with a sponge" (4). This feature has been already noted in many Venetian paintings, including those of Cima (5,6,7), as well as in other Italian paintings of this period (8).

1. The paint medium

The paint medium is oil, but variations in oil content within the different paint layers were detected. Transparent or semitransparent layers, such as copper-resinate or organic pigment glazes, are rich in medium, while the opaque layers show a low proportion of oil medium.

A particularly small amount of oil is contained in the light blue layers of the sky areas and some occasional lead white underpaints which, in addition, contain a protein material: in these areas, the medium is presumably an emulsion.

The use of small amounts of oil medium as well as of emulsions are features shown, in general, by Italian paintings of the period of transition from egg to oil medium (9).

4. The pigments and their mixtures

Most of the pigments occur in heterogeneous mixtures; therefore the results of EDS analysis are complex. But it is possible to combine the results with microscopical examination and microchemical tests to identify the pigments included in the mixture. The complete elemental composition of each pigment was deduced by comparing EDS results for different mixtures including the same pigment. The elemental compositions obtained are listed in the following table.

Elemental composition of pigments (EDS analysis)

Pigment	Elements detected
Gypsum (original)	Ca, S, Si*
Lead white	Pb
Azurite	Cu
Ultramarine	Si, Al, Ca, Na, S, (K, Mg)**
Vermilion	Hg, S
Red lake pigment	Al, (K, Si, Ca, Fe, Mn, Zn, Mg, Na, S)***
Yellow lake pigment	Al, K, Si, Fe, Mg, Ca
Ochre	Fe, Si, Al, Mg, Ca, traces of K
Lead-tin yellow	Pb, Sn
Verdigris	Cu
Copper resinate	Cu
Green earth	Fe, Si, Al, Ca, Mg, K

* Si can arise from clay associated with gypsum in the rock.

** Mg and K are contained, together with Si, Al and a little Ti, in slender white crystals of impurity.

*** Al was detected in all samples examined. The other elements, not always present, are listed according to their frequency of occurrence.

4.1. Blue

Azurite and ultramarine are the blue pigments identified. Azurite (mixed with lead white) only occurs as underpaint of ultramarine layers in sky areas and draperies. Ultramarine also occurs mixed in variable proportions with lead white, as well as pure in the final glaze. Ultramarine over azurite is a feature already observed in other paintings by Cima and other Italian authors of the same period (10).

EDS analysis showed copper in azurite, the only element detectable by EDS in this basic copper carbonate, $2\text{Cu}(\text{CO})_3 \cdot \text{Cu}(\text{OH})_2$. Silicon, aluminium, calcium sodium and sulphur, detected in ultramarine, are the elements contained in lazurite (lapislazuli), a tectosilicate of sodium and calcium with the formula $(\text{Na}, \text{Ca})_8[\text{Si}_4\text{S}_4\text{Cl}]_2(\text{AlSiO}_4)_6$ (11). Potassium and magnesium, also detected in ultramarine, arise from an impurity, a white crystalline silicate which was separated and analysed.

4.2. Red

Vermilion and a red lake pigment appear to be the only reds in the palette of Cima. They are mixed in various proportions, with lead white in addition, in the paint layers of draperies. The use of the red lake pigment is particularly extensive: besides in mixtures with vermillion, it occurs combined with a little lead white in the single coloured layer of a red robe; with a larger proportion of lead white in various underpaints (12).

The elemental composition of vermillion corresponds to cinnabar (mercuric sulphide, HgS).

The elemental composition of the red lake was found to be very complex. Aluminium was always present, among many other more or less frequently occurring elements; this suggested that the dyestuff was incorporated in a support of alumina and the pigment was probably "shearing lake". According to various recipes (13,14) "shearing lake" was prepared as follows: the dyestuff was extracted from shearings of dyed woollen cloths by boiling them in lye prepared from ash of various plants or wood; by treating this extract with roche alum solution the dyestuff was thrown down with the aluminium hydroxide and, after drying, remained incorporated in alumina. Plant ashes can contain great quantities of potassium, calcium, silicon, and also magnesium, iron, and manganese (15). On the other hand, roche alum (basic

potassium-aluminum sulphate, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, is generally associated with various other sulphates containing iron, aluminium and magnesium (16). Therefore the many elements detected in the present lake support might come from the lye or the alum.

4.3. Yellow

The pigments identified in the yellow or yellowish areas are ochre and a yellow lake pigment. Ochre of a rather dark colour, mixed with a little lead white, is the mordant for the gold leaf of S. Peter's halo. Clear yellow ochre occurs, in mixtures with different proportion of lead white, in the brocade robe of S. Peter and in the rock in the *Lamentation*. A yellow lake pigment, mixed with lead white, also occurs in the samples from the same rock area.

The elemental composition of the ochres appears consistent with that of a clay earth whose colour is due to iron oxides.

The support of the yellow lake is rather difficult to identify from its elemental composition. The yellow lake pigments were "giallo santo", prepared from berries of buckthorn, and "arzica" from weld (17). According to antique recipes the dyestuff support was alum and gypsum (18) or alum and "white earth" (19) for giallo santo; calcium carbonate ("travertino finely ground") or alum and lead white for arzica (20). The elements detected did not allow the dyestuff support to be distinguished, but only to exclude some of the possible ones because sulphur and lead are not present.

Another yellow pigment was identified, but only in green areas. This is lead-tin yellow which occurs mixed with verdigris or copper resinate and, in one case, also with green earth. EDS analysis showed that it contains lead and tin and does not contain silicon: therefore it seems to correspond to lead-tin yellow I (lead stannate, Pb_2SnO_4), of the types distinguished by Kühn (21), rather than to type II (approximate formula $\text{PbSn}_2\text{SiO}_7$).

Kühn supposed that lead-tin yellow is the "giallolino" mentioned in Italian antique literature. But the term "giallolino" is used there for different pigments. Moreover, while some of them can correspond to lead-tin yellow II, none seems to correspond to lead-tin yellow I, which seems to have been more commonly used because it is more frequently identified in the works which have been examined. A more detailed discussion on this problem cannot be included here and is the subject of a separate note in the process of preparation.

4.4. Green

Verdigris, copper-resinate and green earth are the green pigments identified. Green earth, mixed with lead white and lead-tin yellow, occurs in the foliage in the *Lamentation*. Verdigris, mixed with lead-tin yellow and/or lead white, occurs in the opaque layers of draperies. Copper resinate, alone or mixed with a little lead-tin yellow, occurs in the semitransparent layers in the same draperies. The addition of lead-tin yellow to verdigris was presumably for the purpose stated in the Bolognese Manuscript: "if you wish it lighter add a little giallolino to it" (22).

The results of elemental analysis are in agreement with the known composition of the pigments. Copper was detected in verdigris (basic acetate of copper) and copper resinate (resinous solution of verdigris). The many elements detected in green earth, which is celadonite or glauconite (23), correspond to the chemical composition of these minerals, both of them phyllosilicates of potassium, calcium, sodium, aluminium, iron and magnesium (24).

5. Paint layer structure

The layer structure is rather simple in the light areas which, however, in only two cases were painted directly in a single layer: a whitish column painted with lead white including traces of ultramarine; a sky area where azurite and ultramarine in a lead white matrix was applied in a single, relatively thick layer.

In most cases the light areas are formed by two layers and, in general, the purpose of underlayer seems to have been to increase luminosity or produce transparency effects (25):

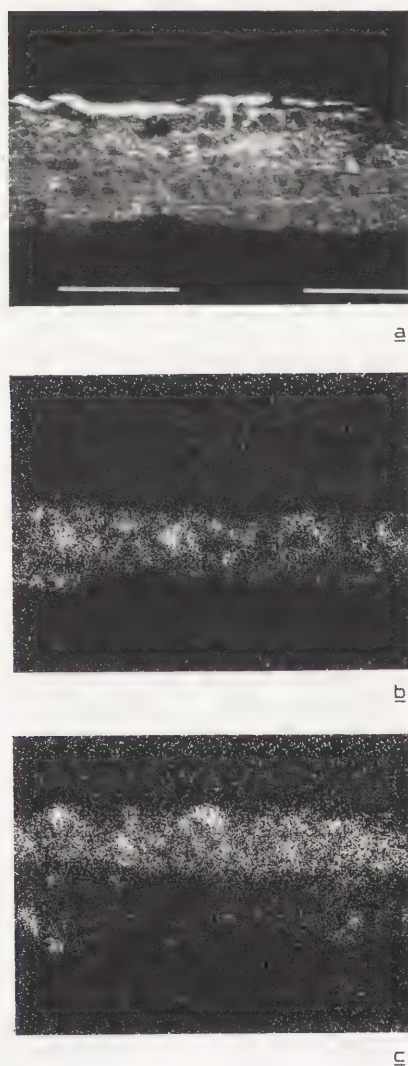
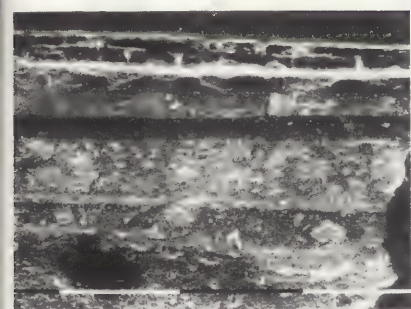
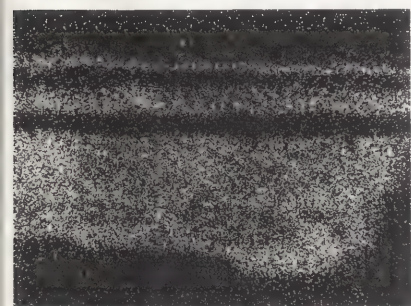


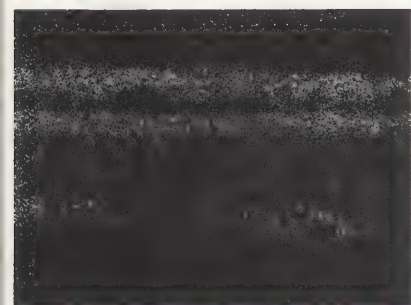
Fig.1
SEM micrograph of the cross-section of a sample from a blue robe (a) and the corresponding elemental distribution of copper (b) and silicon (c), respectively indicating presence of azurite (at the bottom) or ultramarine. The gesso ground is not present in this sample.



a



b



c



d

Fig.2
SEM micrograph of the cross section of a sample from a green robe (a) and the corresponding elemental distribution of lead (b), copper (c), tin (d). The following stratigraphy can be observed:

1. Ground (dark in b,c,d).
2. Thick layer divided in three sublayers containing various amounts of verdigris + lead-tin yellow in a lead white matrix (more white in b than in c and d).
3. A sequence of two copper-resinate layers (dark in b and d, white in c) alternate with two opaque layers similar to those in 2.

- azurite, or red lake, underneath ultramarine (all of them mixed with a high proportion of lead white) in the sky areas;
- white underlayer for the light green of foliage;
- red lake in a white matrix as underpaint of the Madonna's white scarf.

A two layer structure also occurs in the shadow area of the white chair of S. Peter, where the shadow is obtained simply by a brown semitransparent layer over the white paint of the throne.

In the dark areas the paint structure is more complex.

The blue draperies always show the same structure: a first layer of azurite in white matrix (with an higher proportion of white at the bottom); a second opaque layer of ultramarine plus lead white; and, occasionally, a final ultramarine glaze (Fig.1). The layer in the blue cross-sections are always in a sequence from light to dark hue.

Three layers of gradually increasing hue were also observed in the yellow area of the brocade robe of S. Peter. On the contrary, in the rock in the *Lamentation*, also a yellow area, four or five very light (opaque) and darker (transparent) layers are alternated (all of them are very thin): a structure rather difficult to explain.

The most complex paint structure occurs in the green draperies, a feature already observed in other paintings by Cima and by other Venetian authors (5,6,7). The green robes of the Saints, both in *S. Peter in the Chair* and the *Sacred Conversation*, show at least six layers in a sequence not easily interpretable: very light and dark opaque layers alternate; in addition a copper resinate glaze is found as the outermost layer as well as in alternation with the opaque layers (26) (Fig.2).

The structure of the red draperies is relatively simpler and the function of the various layers seems easy to explain. For example:

- the shadow of a robe fold in *S. Peter in the Chair* is painted with a single layer of vermilion with a little ochre;
- the mid-tone of a Saint's robe in the *Sacred Conversation* shows three layers of gradually increasing red hue: two opaque layers containing increasing proportions of vermilion together with lead white and lake, and a red glaze at the top;
- the sample from a light area of a red cloak in the *Lamentation* shows a very simple structure: a white underpaint and a semitransparent layer of red lake with a little lead white (12).

Unfortunately it was not possible to take samples from light, mid-tone and shadow areas of a single red drapery to better understand the painting technique.

6. Conclusion

Dunkerton and Roy, who carried out the most extensive examination of a painting by Cima, observed that "Cima's technique is founded on a detailed and thorough preliminary planning of the design of the works" (5). The same conclusion probably can be reached in the present case, even though the examination was less extensive: the layer structures never showed that a certain area was previously planned to be different.

Once the design had been defined, the paint was built up by the application of a sequence of flat layers, in general of increasing hue (with the exception of the green areas). However, it seems that the first layer of paint of the various colour areas was not totally flat, but rather relatively modulated. As a consequence, saturation of the colour in the shadows was obtained without the application of too many or too thick layers which would prevent transparency of the underpaint.

The use of final glazes also contributes to give depth and richness to the dark colour of the draperies without losing transparency.

The few thin layers in the light areas are certainly intended to allow the light to reflect back from the gesso ground or from the white priming where this is present.

Coloured underpaints were intentionally laid to obtain precise transparency effects. This is the case for the pink layer underneath white paint on the Madonna's scarf and probably, also for the azurite underneath ultramarine, at least in the sky areas. In fact sky areas always show an ultramarine layer at the

top while the underpaint has, alternately, the blue-green hue of azurite or the pink colour of lead white mixed with red lake.

As a general conclusion, the painting technique of Cima appears perfectly designed to produce great coloured brightness and transparency. This characteristic is peculiar for Italian paintings of this period, particularly the Venetian ones, which also show a rather similar technique, at least in regard to the more general characteristics.

Notes and References

1. Information on the treatments which the Sacred Conversation and S. Peter in the Chair underwent in the past were kindly provided by the Soprintendenza per i Beni Artistici e Storici, Milan.
2. Minerali e Rocce, Enciclopedia Italiana delle Scienze (Novara: Istituto Geografico De Agostini, 1972), 501.
3. It had been known for a long time that the gesso ground can be stained and deteriorates if it absorbs oil from the oil paint above, as illustrated by the advice of Cennino Cennini that "oil deteriorates gesso and its medium" (see C. Cennini, Il libro dell'arte cap. CLXXV).
4. G. Vasari, Le Vite, Introduzione: della pittura, cap. XXI (Novara: Istituto Geografico De Agostini, 1967), vol. I, 131-134.
5. J. Dunkerton and A. Roy, "The Technique and Restoration of Cima's The Incredulity of S. Thomas", National Gallery Technical Bulletin, 10 (1986): 4-27.
6. L. Lazzarini, "Lo studio stratigrafico della pala di Castelfranco e di altre opere contemporanee", in Giorgione: La Pala di Castelfranco Veneto, (Milan: Electa Editrice, 1978), 45-59.
L. Lazzarini, "Il colore nei pittori veneziani tra il 1480 e il 1580", Bollettino d'Arte, supplemento 5 (1983): 135-143.
7. H.W. van Os and J.R.J. van Asperen de Boer, The early Venetian paintings in Holland, (Maarssen: Gary Schwartz, 1978).
8. A deliberate reduction of the porosity of the gesso ground, either by heavily sizing the gesso or by applying a separate size layer (or oleaginous layer) is recorded and discussed by P. Hendy, A.S. Lucas and J. Plesters, "The Ground in Pictures", Museum, 11, no. 4 (1978): 245-275.
Notable examples of this practice from works examined in our laboratory include panels by Bartolomeo Montagna (Pietà, Church of SS. Nazaro and Celso, Verona), Ghirlandaio (S. Vincenzo Ferrer, Museo Civico, Rimini), Garofalo (S. Peter and S. Paul, Cathedral of Rovigo), Giovanni Bellini (Pietà, Museo Civico, Rimini), Francesco Francia (Bentivoglio Altarpiece, Church of S. Giacomo, Bologna): see "Analytical Reports" (unpublished), Centro Cesare Gnudi, Bologna; for the Francia panel: R. Rossi-Manaresi, "Notizie sulla tecnica pittorica di Francesco Francia", Alessandro Tiarini e Guercino", Il Carrobbio, rivista di studi bolognesi, III (1977): 339-352.
A distinct size layer above the gesso ground has been observed in Raphael's paintings: see R. Rossi-Manaresi, "Contributi analitici allo studio della Santa Cecilia di Raffaello", in Indagini per un dipinto. La Santa Cecilia di Raffaello (Bologna: Edizioni Alfa, 1983), 253-279; R. Rossi-Manaresi, "A Technical Examination of Raphael's Santa Cecilia with Reference to the Transfiguration and the Madonna di Foligno", in Proceedings of 1983 Princeton Raphael Symposium, (Princeton: University Press, 1990) 125-135.
9. Very small amounts of oil medium occur in another panel by Cima in the Pinacoteca of Parma (see R. Rossi-Manaresi "Esame stratigrafico sul dipinto con la Madonna col Bambino e i SS. Michele e Andrea" in Restauri a cura della Soprintendenza ai Beni Artistici e Storici di Parma e Piacenza, Parma, 1979, as well as in all fifteenth-early sixteenth century paintings analyzed in our laboratory, such as those cited in note 8.
Protein material mixed with oil was used in Garofalo's paintings cited in n.8 and in some areas of the Felicini altarpiece by Francesco Francia: see Rossi-Manaresi, "Notizie sulla tecnica pittorica...", cit. in n.8; R. Rossi-Manaresi and J. Bentini, "The Felicini Altarpiece by Francesco Francia:

Contribution of Technical Analyses to the Solution of a Chronological Problem" in *La pittura nel XIV secolo. Il contributo dell'analisi tecnica alla storia dell'arte*, ed. H.W. van Os and J.R.J. van Asperen de Boer, Atti XXIV Congresso C.I.H.A., Bologna 1979, (Bologna: Editrice CLUEB, 1983), 395-427.

Emulsion of oil in size is the medium of the priming and the white layers in Raphael's *Madonna di Loreto*: see S. Delbourgo, "La matière picturale", in *La Madone de Lorette* (Paris: Éditions de la Réunion des Musées Nationaux, 1979), 60-62.

Emulsion of oil in egg has been detected in Crivelli's paintings: see J. Mills and R. White, "Analyses of Paint Media", *National Gallery Technical Bulletin*, 2 (1978): 71-75 and 11 (1987): 92-95.

The use of emulsion media has also been reported in early Flemish paintings: see L. Kockaert, "Note sur les émulsions de primitifs flamands", *Bulletin de l'Institut Royal du Patrimoine Artistique*, XIV (1973-4): 133-39.

The use of emulsion of oil in white of egg is mentioned in the *Bolognese Manuscript*: see M.P. Merrifield, *Original Treatises on the Arts of Painting*, (New York: Dover, 1967), recipe 201, p.487.

10. Azurite as underpaint for ultramarine has been found in four other paintings by Cima - three of them in the National Gallery, London (see n.5), the fourth in the Pinacoteca of Parma (see Rossi-Manaresi, "Esame stratigrafico...", cit. in n.9).

Ultramarine over azurite is considered a structure peculiar to Flemish painters: see J. Plesters "Ultramarine Blue, Natural and Artificial", *Studies in Conservation*, 11 (1966): 43-50. However it was widely adopted by Italian painters, not only by Cima. It was observed in pictures by Perugino (see D. Bomford et al., "Three panels from Perugino's Certosa di Pavia altarpiece", *National Gallery Technical Bulletin*, 4 (1980): 3-31), Raphael (see S. Delbourgo cit. in n.9), Mantegna (see S. Delbourgo et al., "L'analyse de peinture du Studiolo d'Isabella d'Este", *Annales du Laboratoire des Recherches des Musées de France* (1975): 21-28, and other Venetian painters (see n.7).

The present authors noticed this structure in the paintings by Garofalo, Francia and Raphael cited in notes 8,9. The comparison of the paint on various blue areas on Raphael's works suggests that azurite was layed under ultramarine as a deliberate choice, to obtain very precise effects by transparency rather than as a means of economising on the use of costly ultramarine (see Rossi-Manaresi, articles cit. in n.8). A similar conclusion has also been put forward for Perugino (see Bomford et al. cit. above).

11. *Minerali e Rocce*, op. cit. in n.2, p.295.

12. The simple technique of painting a red robe with a red lake pigment mixed with a little lead white (applied over a lead white priming) also occurs in other Cima paintings (see n.5).

An identical mixture of pigments occurs as underpaint in many Venetian paintings (see n.6) and in works by other Italian painters, for example on Raphael's *Santa Cecilia* and the *Madonna di Foligno* (see Rossi-Manaresi articles cit. in n.8).

Red lake mixed with a high proportion of lead white, directly applied over the gesso ground, is also the single paint layer observed on the Madonna's red dress in the Cavalli altarpiece by Luca Longhi, a painter who Armenini considered "among the great of his time". Longhi's technique, however, is less refined than that of "the Greats" such as Raphael: see R. Rossi-Manaresi, "L'esame scientifico di quadri di Luca Longhi e di altri autori ravennati del XVI secolo" in *Luca Longhi e la pittura su tavola in Romagna nel '500*, (Bologna: Edizioni Alfa, 1982), 215-227.

13. A. Neri, *L'arte vetraria* (Firenze: Marco Rabbuiati, 1661), libro VII, cap. CXVII-CXIX, p.160-164.

14. T. Rossello, *Della summa de' secreti universali* (Venezia: Giovanni Barileto, 1574) parte prima, libro settimo, cap.11.

15. S. Hreglich and M. Verità, "La tecnica di fabbricazione delle vetrate e le indagini analitiche preliminari al restauro" in *La grande vetrata di S. Giovanni e Paolo - Storia, iconografia, restauro* (Venezia: Marsilio Editore, 1982), 157-165.

16. Minerali e Rocce, op. cit. in n.2, p. 182.
17. R.Pietrapaoli and A.Milaneschi, "Gialli" in La Fabbrica dei Colori, (Roma: Il Bagatto 1986), 230-235.
18. Paduan Manuscript, in M.P. Merrifield, Original Treatises..., op. cit. in n.9, recipe 133, p.708-709.
19. Bolognese Manuscript, op. cit. in n.9, recipe 105, p.429.
20. Bolognese Manuscript, ibid, recipe 194, p.483.
21. H.Kühn, "Lead-Tin Yellow", Studies in Conservation, 13 (1968): 7-33.
22. Bolognese Manuscript, op. cit. in n.9, recipe 227, p.503.
23. S.Accorsio, "Verdi" in La Fabbrica dei Colori, cit. in n.17, 271-273.
24. Minerali e Rocce, op. cit. in n.2, 265.
25. This feature is generally seen in Italian panel paintings produced at the turn of fifteenth century. Notable examples are most of the works already mentioned.
26. Multilayered greens frequently occur in Venetian paintings (see n.6) and also in other Italian works of the fifteenth century, for example by Perugino (see Bomford et al. cit. in n.10).

However such a complex structure where glazes alternate with more opaque layers is more rare. Notable examples include the School of Giovanni Bellini Virgin and Child (see n.7) and Cima's The Incredulity of St. Thomas (see n.5). Some hypotheses have been put forward to account for this structure in the latter. However a more general significance of the most complicated green structures, so frequently observed, cannot be elucidated at the present stage of the research. Probably some light could be provided by examining many samples from neighboring areas in the same painting and the comparison of the results for many paintings.

RESUME

Les préparations à base de sulfate de calcium de quelques tableaux italiens peints sur bois aux XIVe, XVe et XVIe siècles, ont été étudiées sur toute leur épaisseur. Un seul enduit ou deux enduits différents ont été mis en évidence par diverses techniques d'observation : coloration spécifique, microscope polarisant, microscope électronique à balayage. L'analyse par diffraction de rayon X a complété ces résultats. Les images en électrons rétrodiffusés ont été exploitées pour chercher à distinguer l'origine naturelle ou artificielle du gypse et de l'anhydrite.

MOTS CLES

Préparation, sulfate de calcium, gypse, anhydrite, microscopie optique, microscopie électronique, biréfringence, peinture italienne.

UTILISATION DES MICROSCOPES OPTIQUE ET ELECTRONIQUE POUR L'ETUDE DES PREPARATIONS BLANCHES DE TABLEAUX ITALIENS SUR BOIS

Naoko SONODA, Elisabeth MARTIN, Alain R. DUVAL
Laboratoire de Recherche des Musées de France
34, quai du Louvre, 75041 Paris Cedex 01

Introduction

Pour préparer leurs tableaux sur bois, les peintres italiens ont utilisé jusqu'au XVIe siècle du sulfate de calcium provenant des carrières de gypse, nom-breuses dans la péninsule (1). Ils avaient à leur disposition le gypse naturel ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) ou des produits obtenus par transformation du gypse : le plâtre de Paris (bassanite $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) (2), l'anhydrite (CaSO_4) (3) et le plâtre mort ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (4).

En 1954, R.J. Gettens et M.E. Mrose (5), et R.A. Bones (6) ont étudié les préparations d'une trentaine de tableaux datés des XIVe et XVe siècles. Dans la préparation réduite en poudre, ils ont identifié par l'observation microscopique en lumière polarisée transmise et par l'analyse en diffraction de rayons X, un mélange d'anhydrite et de gypse dans la plupart des tableaux toscans et du gypse seul, pour les vénitiens.

En partant de ces résultats, nous avons cherché à approfondir les connaissances sur les préparations en Italie par une approche différente en étudiant des coupes stratigraphiques de prélèvements effectués dans toute l'épaisseur de la préparation jusqu'au support.

Observation des échantillons

A partir de l'observation de huit tableaux, il apparaît que l'épaisseur totale de la préparation est en moyenne 1 mm, mais peut varier de 0,5 à 2 mm.

Sous la loupe binoculaire, la préparation de cinq de ces tableaux présente une couleur homogène, d'un blanc plus ou moins jauni à cause du vieillissement de la colle ou d'infiltrations de vernis. Cependant, deux couches différenciées par leur couleur ou leur texture sont parfois visibles. Elles peuvent de surcroît être séparées par une fine couche brunâtre comme sur La Trinité de Bartolo di Fredi (Chambéry, musée des Beaux-Arts).

La réalisation de coupes minces pratiquée au Laboratoire de Recherche des Musées de France depuis 1970 a permis d'étudier des échantillons en lumière transmise polarisée. Dès 1972, M.-C. Gay montrait ainsi que la partie inférieure de certaines préparations présentait une biréfringence plus élevée que la partie supérieure (7). L'observation de coupes minces de la préparation de quelques tableaux a confirmé cet aspect ; par exemple pour La Vierge adorant l'Enfant avec trois anges, saint Joseph et deux bergers de Jacopo del Sellaio, (Ajaccio, musée Fesch) la couche supérieure, peu biréfringente, a une épaisseur de 300 μm , tandis que la couche inférieure fortement biréfringente mesure 500 μm (Fig. 1). Ces observations doivent être rapprochées du fait que l'anhydrite possède une biréfringence plus forte que celle du gypse.

Les préparations contiennent de la colle animale et l'étude par coloration spécifique des protéines (8) (9) permet de localiser le liant et de comparer approximativement les intensités de coloration. La coloration révèle la présence de deux enduits s'ils sont inégalement encollés. L'enduit supérieur peut être plus encollé que l'enduit inférieur, comme dans le Printemps de Botticelli (Florence, musée des Offices) étudié en Italie (10), ou moins encollé comme dans le triptyque florentin de l'église d'Ermenonville. Dans l'enduit supérieur, on peut parfois dénombrer plusieurs fines couches d'environ 50 μm d'épaisseur, visibles après coloration à cause d'une légère augmentation de la concentration de colle à l'interface : sept dans La Trinité de Bartolo di Fredi (Chambéry, musée des Beaux-Arts) et une dizaine dans L'Annonciation avec six saints du Maître du retable d'Arcetri (Avignon, Petit Palais). Dans ce dernier cas, l'enduit supérieur est en effet exceptionnellement épais, de l'ordre de 600 μm . La présence éventuelle d'une couche d'encollage à l'intérieur de la préparation, peut également être mise en évidence par cette technique.

Quelques exemples d'observations de préparations au sulfate de calcium, avec un microscope électronique à balayage ont été déjà publiées (11). Les images obtenues en électrons secondaires permettent d'observer l'état de surface du prélèvement et la forme des grains isolés (Fig. 5). Sur les coupes stratigraphiques, à cause de la présence de colle, le contour des grains ne peut être visualisé qu'en électrons rétrodiffusés. C'est pourquoi, au Laboratoire de Recherches des Musées de France, l'observation de coupes stratigraphiques en électrons rétrodiffusés (12) a été tentée, ce qui a permis de distinguer, sur cinq tableaux florentins, deux couches de matériaux de broyage différent :

Anonymous XVe, triptyque (église d'Ermenonville) (Fig. 2) ; Jacopo del Sellaio, La Vierge adorant l'Enfant avec trois anges, saint Joseph et deux bergers, (Ajaccio, musée Fesch) ; Maître de la Nativité du Louvre, Nativité (Paris,

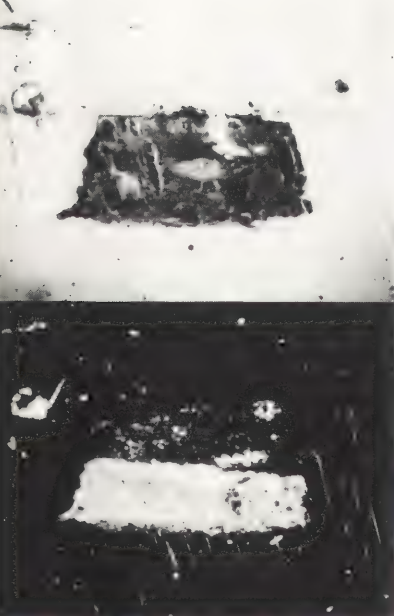


Fig. 1 : Jacopo del Sellaio, La Vierge adorant l'Enfant avec trois anges, saint Joseph et deux bergers, (Ajaccio, musée Fesch). Coupe stratigraphique mince (30 μm) observée en lumière transmise naturelle (en haut) et polarisée (en bas). La différence d'intensité de biréfringence révèle deux zones de préparation, la partie supérieure constituée de gypse, la partie inférieure, constituée d'anhydrite.

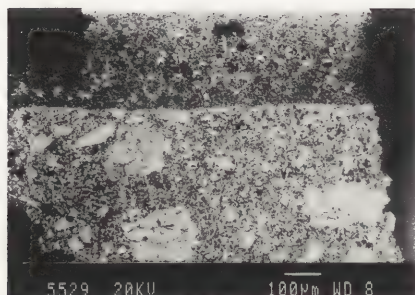


Fig. 2 : Florence XVe, triptyque, (église d'Ermenonville). Coupe stratigraphique épaisse observée au microscope électronique à balayage. Image en électrons rétrodiffusés de l'ensemble de la coupe montrant la différence de broyage entre deux zones de préparation.

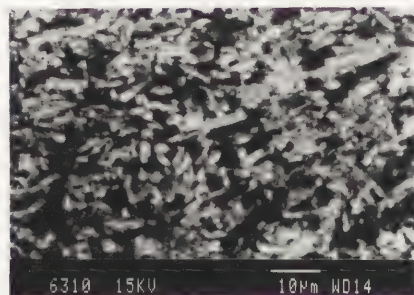
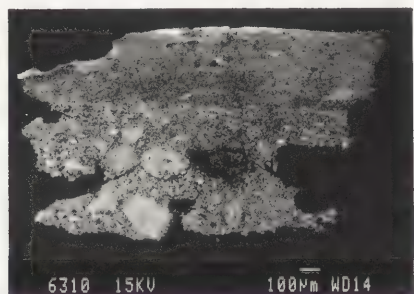


Fig. 3 : Maître de la Nativité du Louvre, Nativité, (Paris, Louvre). Coupe stratigraphique épaisse observée au microscope électronique à balayage.

a) image en électrons rétrodiffusés de l'ensemble de la coupe mettant en évidence la présence de deux zones de broyage différent.

b) image en électrons rétrodiffusés de la zone supérieure de la préparation montrant la forme allongée des grains de gypse.

Louvre) (Fig. 3) ; Maître du retable d'Arcetri, L'Annonciation avec six saints (Avignon, Petit Palais) ; Anonyme XVIe, L'Adoration de l'Enfant (Rouen, musée des Beaux Arts). La couche supérieure est caractérisée par l'homogénéité de la dimension des grains (environ 10 µm) et leur forme allongée, voire aciculaire. En revanche, la morphologie des grains de la couche inférieure est plus hétérogène ; gros amas de petits grains, ou plus rarement assemblages de faisceaux pouvant atteindre une centaine de micromètres parmi des grains trapus beaucoup plus fins.

L'observation d'autres échantillons révèle, sur toute leur épaisseur, un matériau homogène constitué de grains fins de l'ordre de 10 µm dont la forme est souvent allongée : Rome XVe, Antoniazio Romano (entourage de), Le Christ bénissant, Ajaccio, musée Fesch ; Ombrie XVe, La Vierge et l'Enfant dans une gloire de séraphins, Ajaccio, musée Fesch. (Fig. 4).

Toutes ces observations ainsi que l'étude des textes anciens (13) laissent supposer que certaines préparations sont constituées de deux enduits : un enduit blanc, dense, composé de grains homogènes faiblement biréfringents en lumière polarisée et un enduit, d'un blanc parfois moins éclatant, dont les grains fortement biréfringents et de dimension hétérogène, résultent d'un broyage grossier. Il apparaît donc indispensable d'analyser séparément la préparation proche du support et celle proche de la couche picturale.

Composition des enduits

Elle est déterminée par diffraction de rayons X (14). Si les dimensions de l'échantillon inclus le permettent, la poudre à analyser est prélevée sur la coupe stratigraphique épaisse, puisque les deux enduits y sont aisément délimités. Sinon, la séparation est directement effectuée sur le prélèvement initial, sous la loupe binoculaire, ce qui nécessite minutie et habileté.

L'analyse par diffraction X a été pratiquée systématiquement sur les deux côtés des préparations et les résultats obtenus permettent une évaluation semi-quantitative de la composition de chacun des enduits. La quantité relative de gypse et d'anhydrite a été évaluée en comparant les diagrammes de diffraction des préparations avec ceux de mélanges de référence (gypse et anhydrite dans les proportions 1/3, 1/1, 3/1). Les résultats relatifs aux huit tableaux étudiés sont présentés ci dessous :

- Florence XVe, triptyque de l'église d'Ermenonville :
enduit supérieur : gypse
enduit inférieur : anhydrite (> 75%) et gypse (< 25%) ;
- Florence XVe, Jacopo del Sellaio, La Vierge adorant l'Enfant avec trois anges saint Joseph et deux bergers, Ajaccio, Musée Fesch :
enduit supérieur : gypse
enduit inférieur : anhydrite ;
- Florence XVe, Maître de la Nativité du Louvre, Nativité, Paris, Louvre :
enduit supérieur : gypse
enduit inférieur : anhydrite ;
- Florence XVe, Maître du retable d'Arcetri, L'Annonciation avec six saints, Avignon, Petit Palais :
enduit supérieur : gypse
enduit inférieur : anhydrite 50% et gypse 50% ;
- Florence XVIe, L'Adoration de l'Enfant, Rouen, musée des Beaux-Arts :
enduit supérieur : gypse (> 75%) et anhydrite (< 25%)
enduit inférieur : anhydrite ;
- Sienne XVe, Bartolo di Fredi, La Trinité, Chambéry, musée des Beaux-Arts
enduit supérieur : plâtre de Paris
enduit inférieur : gypse 50% et anhydrite 50%.

Contrairement aux exemples précédents, les analyses ont donné le même résultat (gypse) du côté du support et du côté de la couche picturale dans :

- Rome XVe, Antoniazio Romano (entourage de), Le Christ bénissant, Ajaccio, musée Fesch ;
- Ombrie XVIe, La Vierge et l'Enfant dans une gloire de séraphins, Ajaccio, musée Fesch ;

ce qui démontre l'unicité de l'enduit de préparation.

Ces résultats analytiques confirment et précisent les observations effectuées en microscopie optique avec ou sans coloration et en microscopie électronique.

Etude morphologique par microscopie électronique à balayage

L'étude par diffraction de rayons X permet de déterminer la structure cristalline des matériaux mais n'est pas adaptée pour distinguer les trois origines possibles du gypse (naturel, plâtre pris ou plâtre mort) et l'anhydrite natu-

relle de l'anhydrite artificielle. Nous avons tenté de différencier ces divers cas après leur analyse par diffraction de rayons X en recherchant des caractéristiques morphologiques par l'observation des images électroniques. A partir de l'anhydrite naturelle et des trois variétés naturelles de gypse (sélénite, spath satiné, albâtre) (15), nous avons constitué des matériaux de référence :

- gypses et anhydrite naturels broyés ;
- gypses naturels modérément chauffés jusqu'à leur transformation en plâtre de Paris puis recristallisés en gypse :
 - 1) avec un peu d'eau sans agitation (plâtre pris),
 - 2) dans un excès d'eau avec agitation continue (plâtre mort) ;
- anhydrites artificiellement fabriquées par chauffage des gypses naturels au delà de 300°C.

Elaboré comme les matériaux des enduits anciens, avec une granulométrie inférieure à 10 μm , le gypse naturel apparaît sous forme de grains trapus qui ne présentent plus, après broyage de ce matériaux tendre, les plans de clivages et les formes caractéristiques de la variété d'origine. En revanche, si le gypse a été obtenu par réhydratation (plâtre mort), nos essais montrent qu'il se présente sous forme de fines aiguilles plus ou moins brisées, quelle que soit la variété de gypse d'origine (Fig.5). Les mêmes cristaux en aiguilles sont observés dans le cas du plâtre pris, mais ils sont beaucoup plus longs et bien enchevêtrés en masse compacte. L'homogénéité du broyage, la forme et la finesse des grains de gypse observés sur les images en électrons rétrodiffusés de la partie supérieure ou de la totalité de la préparation de certains des tableaux examinés sont comparables aux caractéristiques du plâtre mort et permettent de conclure à une origine artificielle, obtenue par réhydratation.

En 1954, par observation de la poudre au microscope polarisant, R.J. Gettens et M.E. Mrose remarquaient la similitude de forme entre les cristaux d'anhydrite artificielle et ceux présents dans les préparations anciennes. Les références d'anhydrites artificielles broyées au laboratoire, présentent sur les images électroniques, des morphologies particulières ; petits grains qui peuvent être regroupés en amas ou assemblages de faisceaux. Au contraire, les fragments d'anhydrite naturelle, même finement broyés (10 μm), conservent leur structure feuilletée à trois clivages orthogonaux. Ces observations tendent à prouver que l'anhydrite présente dans les préparations blanches des tableaux anciens a été obtenue artificiellement.

Le plâtre de Paris (ou bassanite), utilisé dans la partie supérieure de la préparation de La Trinité de Bartolo di Fredi, ne présente pas des images en électrons rétrodiffusés très caractéristiques. Le plâtre ne s'est pas hydraté en gypse comme cela eût semblé normal en présence d'un liant aqueux ; la présence de colle et la température relativement élevée du matériau chauffé au bain-marie avant l'application semble avoir retardé la prise du plâtre dont la structure cristalline est demeurée inchangée. Une vérification de ce fait a été effectuée au L.R.M.F. : 8 g de plâtre de Paris ont été mélangés avec 20 cc de solution de gélatine à 10% et l'ensemble a été étalé sur une planche. L'analyse par diffraction de rayons X, après un an et demi de séchage, montre qu'il s'agit toujours de plâtre de Paris.

Conclusion

Dans les huit panneaux italiens étudiés, nous avons pu caractériser selon le cas un seul enduit ou deux enduits différents par diverses techniques d'observation : coloration spécifique, microscope polarisant et microscope électronique à balayage. La composition de chaque enduit peut être évaluée approximativement (majorité de gypse ou d'anhydrite) en observant l'intensité de la biréfringence en lumière polarisée transmise ou de façon plus précise par diffraction de rayons X. Les résultats recoupent les textes anciens et en particulier celui de Cennino Cennini (13) ; l'enduit supérieur finement broyé à base de gypse correspond au "gesso sottile" et l'enduit inférieur à gros amas à base d'anhydrite correspond au "gesso grosso".

On constate que, contrairement aux conclusions de R.J. Gettens et M.E. Mrose, le gypse artificiel seul est aussi utilisé en dehors de Venise et constitue le matériau le plus proche de la surface dans sept des huit exemples que nous avons présentés. Dans les cas où la morphologie des cristaux est bien caractéristique, l'étude des images en microscopie électronique à balayage (électrons rétrodiffusés) permet de déterminer si le gypse et l'anhydrite sont d'origine naturelle ou artificielle lorsque la concentration en colle n'est pas trop importante pour gêner la lisibilité des documents. Les résultats expérimentaux peuvent être alors valablement comparés aux textes anciens où l'obtention du gypse par réhydratation est effectivement décrite.

Ces premiers résultats nous ont encouragés à appliquer cette méthode à une cinquantaine de tableaux italiens actuellement en cours d'étude. Les résultats définitifs seront publiés ultérieurement.

REMERCIEMENTS

Nous adressons nos vifs remerciements à l'Institut de Conservation Getty pour son aide généreuse, à M.-C. Gay pour sa collaboration dans la première phase de ce travail et à D. Bagault pour les tirages photographiques.

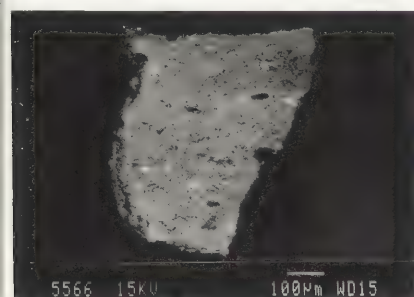


Fig. 4 : Ombrie XVIe, La Vierge et l'Enfant dans une gloire de séraphins, (Ajaccio, musée Fesch). Coupe stratigraphique épaisse observée au microscope électronique à balayage. Image en électrons rétrodiffusés de l'ensemble de la coupe montrant l'homogénéité du broyage dans toute l'épaisseur.



Fig. 5 : Gypse artificiel obtenu par réhydratation du gypse naturel modérément chauffé jusqu'à l'état de plâtre de Paris. Image en électrons secondaires.

NOTES

- 1) R.J. Gettens, " A Visit to an ancient gypsum quarry in Tuscany", Studies in Conservation, vol 1, 1954, pp. 190-192.
- 2) Chauffé entre 150 et 180° C, le gypse $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ se transforme en plâtre de Paris ou bassanite $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.
- 3) Chauffé entre 180 et 300° C, le gypse se transforme en anhydrite CaSO_4 réhydratable qui se convertit rapidement en plâtre de Paris au contact de l'humidité ambiante. Au delà de 300° C, il se transforme en anhydrite stable.
- 4) En présence d'eau, le plâtre de Paris se réhydrate ; on obtient une masse solide formée d'un enchevêtrement de fines aiguilles de gypse. C'est la prise du plâtre. En augmentant la quantité d'eau et en agitant continuellement le mélange, on empêche la croissance des cristaux de gypse et leur enchevêtrement : et on obtient, après évaporation de l'eau, non pas une masse solide (plâtre pris), mais une poudre de gypse n'ayant plus la capacité de prise, que l'on appelle plâtre mort.
- 5) R.J. Gettens, M.E. Mrose, "Calcium sulfate minerals in the ground of italian paintings", Studies in Conservation, vol 1, 1954, pp. 174-189.
- 6) R.A. Bones, "The analysis of calcium sulfate grounds by an X-Ray diffraction process", Studies in Conservation, vol 1, 1954, pp. 193-195.
- 7) M.-C. Gay ("Application de la méthode des colorations sur coupes minces à l'étude des liants de quelques peintures italiennes du XIVe et du XVe siècles", Conservation of paintings and the Graphic Arts, Congrès de Lisbonne, IIC, 1972, pp. 705-713) a ainsi distingué deux couches de gesso dans la préparation du tableau de Macchiavelli, La Vierge à l'Enfant (Avignon, Petit Palais). Elle a attribué cette distinction à la différence d'orientation des grains de sulfate de calcium. Il s'est révélé, lors de nos analyses, que c'est la différence de composition entre les deux couches qui en est la cause, l'anhydrite étant plus biréfringente que le gypse.
- 8) M.-C. Gay, "Essai d'identification et de localisation des liants picturaux par des colorations spécifiques", Annales du L.R.M.F., 1970, pp. 8-20.
- 9) E. Martin, "Contribution à l'analyse des liants mixtes", Comité pour la Conservation de l'I.C.O.M., 5ème réunion, Zagreb, 1978/20/8.
- 10) Catalogue de l'exposition Metodo e Scienza, Florence, les Offices, juin 1982 - janvier 1983, p.226.
- 11) J. Dunkerton, A. Roy, "The technique and restoration of Cima's "The Incredulity of S. Thomas"", National Gallery Technical Bulletin, vol.10, 1986, pp. 4-27.
- 12) Microscope JEOL JSM840. Les échantillons ont été recouverts d'une couche de carbone afin d'assurer la conduction électrique.
- 13) Cennino Cennini, "le livre de l'art" traduit pas Victor Motez, Paris, 1982, pp. 83-88.
- 14) Chambre Debye-Scherrer, anticathode de fer, 35 KV, 12 mA.
- 15) J. Deville, "Le Gypse", Minéraux et Fossiles, n° 128, mars 1986, pp. 37-46.

RESUME

Ce travail a pour objectif l'étude de la technique picturale et des matériaux utilisés dans un ensemble de six peintures attribuées à Maître Athayde, peintre et doreur brésilien qui a vécu et travaillé dans la région de Ouro Preto, Minas Gerais, Brésil, pendant la deuxième moitié du XVIIIème siècle et le début du XIXème. Maître Athayde est, avec Aleijadinho, le plus important artiste de la période rococo à Minas Gerais. Les méthodes d'analyse utilisées comprennent des méthodes physicochimiques (tests de solubilité, tests de coloration, microchimie, diffraction des rayons X) ainsi que l'analyse stratigraphique de coupes minces. Les résultats obtenus, comme par exemple la vérification de l'utilisation surtout des liants huileux (émulsion protéine/huile) et l'occurrence de préparations blanches et d'autres brunes sont des éléments très importants pour la caractérisation de la méthode de travail employée par l'artiste.

ETUDE TECHNIQUE DES SIX PEINTURES ATTRIBUEES A MAITRE ATHAYDE, LE PEINTRE LE PLUS IMPORTANT DE LA PERIODE BAROQUE/ROCOCO A MINAS GERAIS, BRESIL

Luiz A.C. Souza, Marília O.S. Pereira, Centro de Conservação e Restauração de Bens Culturais Móveis (CECOR) - Universidade Federal de M.G. - Av. Ant^o. Carlos, 6627 - Belo Horizonte - Brasil - 31270

I. Introduction

La période coloniale au Brésil a duré 306 ans, de l'année 1500 à l'année 1806, quand le Roi de Portugal et sa cour se sont transférés à cette colonie, à cause de l'imminence de l'occupation du Portugal par l'armée de Napoléon.

L'occupation portugaise au Brésil s'est surtout concentrée d'abord au littoral, à cause de l'exploitation du bois du Brésil et, vers la fin du XVIème siècle, de la canne à sucre.

Au début du XVIIème siècle des expéditions se sont organisées partant de São Paulo vers l'intérieur du Brésil, à la recherche d'or et de pierres précieuses. Ces expéditions ont contribué à la formation de petites villes dans les régions où elles passaient, et c'est dans ce contexte qu'eut lieu l'occupation de la région actuelle de Ouro Preto (Or Noir), ville dans les montagnes de l'état de Minas Gerais.

La découverte de l'or en abondance à Vila Rica (Ville Riche, ancien nom de Ouro Preto) a attiré l'attention d'autres expéditions qui ont contribué à la formation de nouvelles villes dans la région. La production de l'or comptait sur le travail des esclaves noirs et la région de Vila Rica est devenue, au XVIIIème siècle, l'une des villes les plus riches du pays, autant du point de vue matériel que culturel (1).

La production artistique était consacrée surtout à la demande des ordres religieux (pour la décoration des églises) et des grands propriétaires de terres (pour la décoration de chapelles de fermes).

Ce bref aperçu historique sert à donner une idée de la réalité de l'époque d'or à Vila Rica. La richesse de l'architecture et de la peinture baroque et rococo de la région de Ouro Preto est très bien décrite dans l'oeuvre de Mr. Bazin (2,3).

Le sujet de ce travail concerne l'étude des matériaux constitutifs et de la technique picturale de six peintures sur toile attribuées à Maître Athayde, peintre et doreur brésilien (1762-1830) né à Mariana, ville à 10 km de Ouro Preto. Athayde est considéré le peintre le plus important de la période rococo à Minas Gerais (4,5). Ses travaux de peinture comprennent la peinture sur toile ou sur panneau. Son chef d'oeuvre c'est la peinture de perspective de 300 m² au plafond de la nef de l'église de São Francisco de Assis, à Ouro Preto, déjà étudiée par notre laboratoire (6).

Les oeuvres étudiées dans ce travail sont les suivantes:

1. São Camilo de Lélis;
2. São Francisco de Paula;
3. Santo Inacio de Loyola;
4. São Nicolau Tolentino;
5. São Pedro Apóstolo;
6. São Thomas Aquino.

Cet ensemble a été trouvé dans la chapelle d'une ferme coloniale dans la ville de São Domingos do Prata, à Minas Gerais, où elles sont restées jusqu'à 1978, quand le gouvernement de l'état les a achetées pour qu'elles fassent partie de la collection du Museu Mineiro, à Belo Horizonte, Minas Gerais.

II. Partie ExperimentaleII.1) Prélèvement d'échantillons

Les échantillons des peintures ont été prélevés suivant les possibilités d'après l'état de conservation des tableaux, ainsi qu'en tenant compte des diverses couleurs employées par l'artiste.

Dans chaque peinture on a prélevé une moyenne de cinq points différents. Les points d'échantillonnage ont été marqués sur une photo en couleur.

II.2) Méthodes d'analyse

Les échantillons prélevés des peintures ont été analysés selon les techniques suivantes:

- a - Test de solubilité dans l'eau, effectué sous la loupe binoculaire (8);
- b - Vérification à la loupe binoculaire de la réaction de l'échantillon à une goutte de solution de KOH à 10% dans l'eau (9);
- c - Identification microchimique des pigments et charges (10);
- d - Elaboration de coupes minces et postérieure observation microscopique (100%) pour l'étude de la stratigraphie;
- e - Tests de coloration des coupes minces au noir d'amidon; 2 pour la localisation des liants protéiques (11);
- f - Tests de coloration des coupes minces au noir Soudan pour la localisation des liants huileux (12);
- g - Analyse des coupes minces à la microsonde électronique de Castaing (13);
- h - Diffraction des rayons X à la chambre de Debye-Scherrer;
- i - Identification des fibres du support par coloration au Néocarmin W et par observation microscopique (100x) (14).

II.3) Résultats et discussion

II.3.a) Support

Les supports utilisés pour les six peintures sont constitués de fibres de lin (*Linum usitatissimum*), identifiées selon la méthode i ci-dessus.

II.3.b) Stratigraphie

L'étude stratigraphique a permis de séparer les peintures étudiées en deux groupes principaux, selon la couleur de la base de préparation:

Groupe A) Tableaux 1 et 2: préparation blanchâtre, appliquée directement sur le support encollé; épaisseur d'environ 100 μ m.

Groupe B) Tableaux 3 à 6: préparation brunâtre (100 μ m) appliquée sur une couche jaune orange (5-20 μ m) celle qui se trouve sur le support de lin encollé. L'interface préparation-couche picturale se présente très uniforme si l'on compare à celle du groupe A.

Les couches picturales des six peintures présentent à peu près les mêmes caractéristiques, c'est-à-dire une couche de peinture d'épaisseur variable de 15 à 50 μ m appliquée sur la préparation, suivie d'un vernis (5 μ m) qui est devenu brunâtre à cause du vieillissement.

L'observation microscopique des bases de préparation des peintures du groupe B nous permet de vérifier une différence de tonalité entre ses parties inférieure et supérieure. Dans toutes les coupes la partie inférieure de la préparation se présente plus brune que la partie supérieure. On suppose que l'artiste a dû utiliser des relations pigment-liant différentes, en utilisant une plus grande quantité de pigment brun dans la partie inférieure de la base de préparation. L'aspect très lisse de la préparation brune permet de supposer qu'elle a été bien polie avant l'application de la couche picturale. Les bases de préparation blanches ne présentent pas ces caractéristiques.

II.3.c) Liants, vernis, pigments et charges

Les tableaux I et II ci-dessous présentent les résultats trouvés en ce qui concerne la nature de liants et vernis utilisés dans les peintures, ainsi que les pigments et charges rencontrés. Les lettres qui sont à la dernière colonne correspondent aux méthodes d'analyse employées.

<u>Materiau</u>	<u>Groupe A</u>	<u>Groupe B</u>	<u>Methode</u> (Voir II.2)
vernis	protéine	protéine	e
liant	émulsion huileuse avec peu de protéine	émulsion huileuse avec peu de protéine	a,b,e,f

Tableau I - Nature des vernis et liants retrouvés dans les peintures des groupes A et B et respective méthode d'analyse employée (voir II.2).

<u>Pigment</u>	<u>Groupe A</u>	<u>Groupe B</u>	<u>Methode</u> (Voir II.2)
blanc	blanc de plomb carbonate de Ca	blanc de plomb carbonate de Ca	c,g,h c,g,h
bleu	bleu de Prusse	bleu de Prusse	c,g
brun	oxydes de fer —	oxydes de fer brun Van Dyck	c,g c,g
rouge	oxydes de fer cinabre	oxydes de fer cinabre	c,g c,g
vert	verdigris	—	c,g

Tableau 2 - Pigments et charge rencontrés dans les peintures des groupes A et B et respective méthode d'analyse employée (Voir II.2).

Dans les peintures du groupe A on vérifie que la base de préparation est constituée d'un mélange de blanc de plomb et de carbonate de calcium, pendant que dans les peintures du groupe B l'artiste a utilisé un mélange blanc de plomb-carbonate de calcium-brun Van Dyck. Les tests de coloration au noir d'amidon et au noir Soudan n'ont pas donné d'éléments pour que l'on puisse déterminer la nature du liant de la couche jaune-orange qui se présente entre la préparation et le support dans les peintures du groupe B. L'analyse de cette couche à la microsonde électronique de Castaing a révélé qu'elle se compose de pigments de fer.

L'artiste a préparé toutes ses couleurs par l'addition du pigment coloré dans un mélange de blanc de plomb-carbonate de calcium, sauf dans le cas du pigment vert de cuivre où il n'y a que les grains du pigment vert et de blanc de plomb.

Il faut aussi remarquer que pour la représentation du soleil sur la peinture 2 l'artiste a utilisé du blanc de plomb pur dans un liant protéique, certainement pour éliminer l'influence du jaunissement qui serait causé par le vieillissement de l'huile. L'observation de la coupe mince du soleil mentionné ci-dessus permet de vérifier que la couche blanche est beaucoup plus blanche que tous les autres blancs trouvés dans les autres peintures.

L'utilisation de la microsonde de Castaing pour l'analyse de la base de préparation des peintures du groupe B ne montre qu'une faible concentration de Fe et Mn en relation à la concentration de Pb et Ca, ce qui ne nous permettrait pas d'expliquer la couleur brune que l'on y trouve. L'analyse de diffraction des rayons X des échantillons à la chambre de Debye-Scherrer ne montre que la présence du blanc de plomb et de carbonate de calcium. La présence du brun Van-Dyck n'a pu être détectée qu'à l'aide d'exams microchimiques pour Fe et Mn et des tests de solubilité dans le KOH à 10% dans l'eau. C'est ce pigment, qui contient seulement à peu près 10% de matière inorganique qui est le responsable de la couleur brune de la préparation (15).

Les méthodes d'analyse employées dans ce travail ne nous ont pas permis de déterminer quelle huile et quelle protéine ont été utilisés, cependant on espère avoir dans le futur des conditions d'analyser ces matériaux par chromatographie en phase gazeuse, spectrométrie infra-rouge et d'autres techniques plus précises.

IV. Source des matériaux

Les matériaux retrouvés dans les six peintures étudiées se trouvent, à l'exception du carbonate de calcium et des oxydes de fer, dans un liste de commande élaborée par Maître Athayde à l'époque de l'exécution de la peinture du plafond de l'église de São Francisco de Assis (16).

La région de Ouro Preto est très riche en pigments de fer et c'est une habitude des artistes de la région d'utiliser ces pigments dans leurs peintures. Cela nous permet de supposer que les terres d'oxydes de fer soient de provenance de la région. Les autres matériaux utilisés doivent venir d'Europe puisque la liste est adressée à des magasins à Rio de Janeiro, le port d'entrée des produits étrangers au Brésil.

V. Conclusions

Les résultats obtenus dans ce travail nous permettent de connaître du point de vue technique, les caractéristiques propres de ces oeuvres attribuées à Maître Athayde en ce qui concerne les matériaux utilisés pour leur exécution. Des six peintures étudiées on a trouvé deux qui ont la préparation blanche et quatre avec préparation brune. Les liants utilisés sont surtout des liants huileux (émulsion huile/protéine) et les pigments dans presque tous les cas se trouvent mélangés avec du blanc de plomb et du carbonate de calcium. Le vernis utilisé est un vernis de nature protéique.

Il y a encore dans la région de Ouro Preto beaucoup d'autres oeuvres de peinture, de dorure et de carnation attribuées à Maître Athayde qui seront, dans un futur proche, objets d'étude dans notre laboratoire. On espère, de cette façon, contribuer à la connaissance plus approfondie de l'époque baroque et rococo à Minas Gerais.

VI. References

- 1 - Blume, K., La ciudad que fué antaño la más rica del mundo, in Humboldt, 86 (1975), 75-79;
- 2 - Bazin, G., L'Architecture Religieuse Baroque au Brésil, Paris, Plon, 1956;
- 3 - Bazin, G., Aleijadinho et la sculpture baroque au Brésil, Paris, Le Temps, 1963;
- 4 - Menezes, I. P. de, Manoel de Costa Athayde, Ed. Arquitetura, no. 1, Belo Horizonte, 1965;
- 5 - Oliveira, M.R., Barroco, Belo Horizonte, Imprensa Universitária, 12, 12 (1981), 171-180;
- 6 - Moresi, C.M.D., Estudo dos materiais pictóricos da principal obra do Mestre Ataíde, Thèse de M. Sc., Departamento de Química, Universidade Federal de Minas Gerais, Belo Horizonte, 1988;
- 7 - As Seis Telas de Athaide, Museu Mineiro, Belo Horizonte, 1986, (catalogue d'exposition);
- 8 - Kleiner, L.M., Contribution à l'analyse des liants, adhésifs, et vernis anciens, in Studies in Conservation, 13 (1968), 105-121;
- 9 - Mills, J.S. & White, R., The Organic Chemistry of Museum Objects, Butterworths, London, 1986, p. 29;
- 10 - Gettens, R.J., History, Description and Microscopic Identification of the pigments used in painting, Notes Personnelles, Washington, s.d.;
- 11 - Martin, E., Some improvements in Techniques of analysis of Paint Media, in Studies in Conservation, 22 (1977), 63-67;
- 12 - Gay, M.C., Essais d'identification et de localisation des liants picturaux par des colorants spécifiques sur coupes minces, in Laboratoire de Recherches des Musées de France, (1970), 8-24;
- 13 - Hanlan, J., The scanning electron microscope and microprobe application to conservation and historical research, in ICOM Committee for Conservation, 4th triennial Meeting, Venice, (1975), 74/4/s;
- 14 - Guerra, R.A., Identificación de Fibras Textiles, Barcelona, Blume, (1968);
- 15 - Gettens, R. & Stout, G.L. Painting Materials: A Short Encyclopaedia, Dover Publ. Inc., New York, (1966), p. 168;
- 16 - Trindade, C.R., São Francisco de Ouro Preto; crônica narrada pelos documentos da Ordem, Rio de Janeiro, Publicações da Diretoria do Patrimônio Histórico e Artístico Nacional, Rio de Janeiro 17 (1951), 399-411.

VII. Matériaux

Neócarmin W - Fesago Chem., Fabrik Dr. Gossler G.m.B.H.
 D 6902 Sandhausen b Heildelberg
 Carl-Benz-Str. 18 - téléphone: (06224) 4820

Remerciements

L'auteur (L.A.C.S.) veut bien remercier Mme. Liliane Masschelein-Kleiner, Directeur de l'Institut Royal du Patrimoine Artistique, ainsi que le staff du laboratoire pour l'utilisation des équipements et discussions pendant la réalisation de ce travail, réalisé à l'IRPA comme partie du stage de perfectionnement effectué par l'auteur. Nous voudrions aussi remercier la CAPES, organisme du gouvernement brésilien qui a bien donné l'appui financier pour l'exécution de ce travail. A Mme. Beatriz Coelho, Mr. Edson Motta Jr., et Mme. Marilka Mendes pour les discussions concernant ce travail.

ABSTRACT

The possibility of application of the luminescence method to the identification of glutin glues as ingredients of binders used in painting is discussed. The procedure of the analysis is described. A suggestion is made on the possibility of application of this technique to a study of tryptophane-containing binders - the egg white and yolk, casein.

KEYWORDS

Luminescent analysis, tryptophane-containing binder, glutin glue, fluorescence, fluorescence spectrum.

LUMINESCENCE STUDY OF PROTEIN BINDERS USED IN PAINTING

Tseitlina M., Kozhukh N.
Belspetsproektrestavratsya Institute,
143 M.Gorky St., Minsk 220100,
U S S R

Introduction

This work has resulted from the investigations of protein binders used in painting and estimation of the efficiency of the luminescence method in such investigations. Although much attention is paid to studying binders in recent years, their analysis is still a complicated problem. The main difficulty consists in the fact that in the course of natural ageing the protein binder undergoes considerable physico-chemical changes which are insufficiently known. The methods used at present (thin-layer chromatography, IR-spectroscopy, electrophoresis, analysis of protein binders by the amino-acid analyser, etc.) allow to solve this problem more or less successfully. However, each of these methods is not free of disadvantages; In addition to the existing methods we present a simple and highly sensitive luminescent method of analysis of protein binders.

First attempts of luminescent analysis of oils, resins, waxed and varnishes were made as early as the 1920's. Eibner /9/ continued studies in this direction and found that some binders taken in their pure form have luminescence of different colour and intensity. In spite of his own statement, however, that "the primary importance of UV-light for painting consists in... identifying the binders", his investigations in this direction proved prospectless /1/. The main reason of this was the imperfection of luminescent equipment of that time. In his review "Identification of binders in painting" presented at a regular conference of the International Institute of Conservation held in Lisbon in 1972, Mills expressed doubts about recent reports on surprising progress in identification. Analyzing the methods applied, Mills pointed out a possibility of detecting proteins by using the fluorescent antibody technique which is only now coming into existence /2/.

In the 1950-1960's the luminescent analysis and luminescent equipment began to develop rapidly. A lot of investigations of protein luminescence were carried out at that time. Weber and Teale /8/ as well as Vladimirov and Konev studied ultraviolet fluorescence of proteins. It was shown that intrinsic luminescence of proteins is due to the aromatic amino acids present in proteins: tryptophane, tyrosine, phenylalanine. Maxima of luminescence spectra of these amino acids are at 348, 303 and 282 nm, respectively; quantum yields of luminescence are 0.20, 0.14 and 0.04, respectively /3/.

Fluorescence of phenylalanine is only observable in the absence of tyrosine and tryptophane and that of tyrosine - in the absence of tryptophane in proteins. Fluorescence spectra of proteins are not identical to spectra of the equimolar mixture of their amino-acids and are therefore dependent on the structural organization of proteins.

I. Experimental studies

At the first step of our investigations we studied fluorescence and fluorescence excitation spectra of aqueous solutions of the egg white and yolk, casein, fish, bone and hide glues, as well as aqueous solutions of samples from mural and easel painting. The solutions were preliminary thermostated at 40°C. Fluorescence and fluorescence excitation spectra were recorded on Fica-55 MK-P and Jobin Yvon JY3 CS spectrofluorometers (France).

Fluorescence spectra of the egg white and yolk and casein are bands with a maximum at 333-334 nm ($\lambda_{ex.} = 290-300$ nm) /Fig.1/ which are due to the fluorescence of tryptophane present in these proteins.

Fluorescence spectra of glues without tryptophane are identical: fluorescence maxima are at 308-310 nm ($\lambda_{ex.} = 280$ nm) and in the region of 415-440 nm ($\lambda_{ex.} = 340$ nm) /Fig.2/. Fluorescence at 308nm is emitted by tyrosine. The fluorescence spectrum in the longer wave region has an involved character; maxima at 415-420 nm and 435 nm. The positions of maxima at 415-440 nm depend on the excitation wavelength. This fluorescence is possibly emitted by cross-linked molecules resulting from oxi-

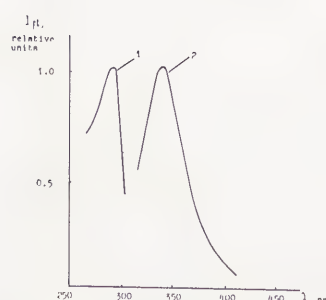


Fig.1 Fluorescence and fluorescence excitation spectra of the egg white aqueous solution:

1- $\lambda_{ex.} = 292$ nm

2- $\lambda_{fl.} = 334$ nm

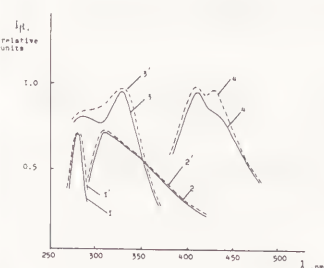


Fig. 2 Fluorescence and fluorescence excitation spectra of bone (—) and hide (---) glue water solutions
 1, 1' $\lambda_{fl.} = 310$ nm
 2, 2' $\lambda_{ex.} = 280$ nm
 3, 3' $\lambda_{fl.} = 420$ nm
 4, 4' $\lambda_{ex.} = 340$ nm

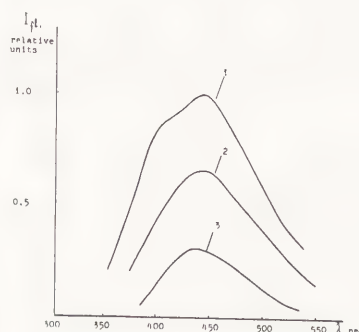


Fig. 3 Fluorescence spectra of aqueous solutions of paintings ($\lambda_{ex.} = 340$ nm):

1. primer of the sculpture of Virgin Mary
2. pink (ochre) layer of paint in the murals of the Church of Stanislaw (Mogilev)
3. pink (ochre) layer of paint in the murals of Uspensky Cathedral (Mstislav)

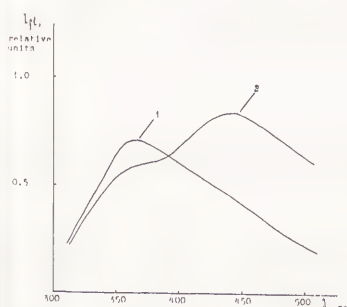


Fig. 4 Fluorescence spectra of paint of the icon of St. Stephen.

dation of tyrosine residues to reactive quinoid structures capable of covalent binding to the neighbouring functional groups /4/.

II. Applied studies

Fluorescence spectra of aqueous solutions of samples (primers of icons from collections of Byelorussian museums, mural painting of Uspensky Monastery /Mstislavl, 18 c/, Church of Stanislaw /Mogilev, 18 c/ and others) contain a band with a maximum in the region of 415-440 nm ($\lambda_{ex.} = 340$ nm) /Fig.3/ that may testify the presence of glutin glues in the binder. We failed to register fluorescence ($\lambda_{ex.} = 340$ nm) of aqueous solutions of the layers of paint from murals of the Cathedral of Sofia (Polotsk, 12th c), Grand Cathedral of Belchitsky Monastery (Polotsk, 13th c), Cathedral of Christmas (Slavgorod, 18th c.) which indicates the absence of glutin glues in them. The luminescent analysis data were confirmed by ion exchange chromatography performed on Fision 50 x 8 plates (Hungary) /5/. Besides, the amino acid composition of the binder of unrestored paintings was studied on an LKB-320 amino-acid analyser (Sweden). It was found that the murals from Slavgorod had the egg as their binder, whereas vegetable protein was used as binder of the murals from Polotsk.

Also, an attempt was made to register fluorescence of tryptophane-containing binders in aqueous solutions of paintings. Thin-layer chromatography allowed to detect the egg in the binder of the icons of St. Stephen (17th c), Archangel Michael (1st half of the 17th c) and others as well as a layer of blue paint in the murals of Trinity Cathedral (Alexandrov) /6/. Unfortunately, no tryptophane fluorescence was registered in the aqueous solutions. In our opinion, that was because of poor water solubility of the aged tryptophane-containing proteins.

At present a study is being carried out of the fluorescence spectra of paintings in 8 M urea which facilitates dissolution of aged proteins.

It is known that denaturing of the egg white and yolk and casein in 8 M urea leads to a shift of the fluorescence spectra into the long wave region and to their almost identical position with a maximum at 350 nm ($\lambda_{ex.} = 295$ nm) /7/. The positions of the fluorescence maxima of glutin glues in 8 M urea do not change.

In two samples: the layer of blue paint (Trinity Cathedral, Alexandrov) and the layer of paint of the icon of St. Stephen (17th c) we registered fluorescence with a maximum at 350 nm ($\lambda_{ex.} = 295$ nm) /Fig.4/. In our opinion, this fluorescence is due to the presence of a tryptophane-containing binder, but further investigations are needed to identify the compounds emitting fluorescence in this region.

Thus it is possible to draw a conclusion on the possibility of identification of glutin glues by the luminescence method. Further studies concerning the application of this method to identification of tryptophane-containing binders are required. The method has certain advantages in comparison to other techniques: high sensitivity, reliability, simplicity in use.

References:

1. Grenberg Yu.I. Assays on the history of technical and technological studies of painting. - Soobshchenia VTSNILKR. M., 1971. V.27. P.60.
2. Mills J.S. Identification of binders in painting. Introduction. - Restavratsia i khranenie muzeinykh khudozhestvennykh tselestei. M., 1974, Vyp.417.
3. Vladimirov Yu.A. Photochemistry and luminescence of proteins. M., 1965
4. La Belle F.S., Parel G.J. Gerontology. 1965. V. 20, P. 54
5. Deveny T., Gergij Ya. Amino-acids, peptides, proteins. M., 1976
6. Striga I.I., Kozhukh N.M. Culture and art in the USSR. - Ser. Restavratsiya pamyatnikov istorii i kultury: Express-inform. 1988. Vyp.7 p. 1-4.
7. Chernitsky E.A. Luminescence and structural lability of proteins in solution and cell. Minsk 1972
8. Weber G., Teale F.W.J. In: The Proteins. Aced. Press. N.Y. 1965. v.3 P.473
9. Bibner A. Les rayons ultra-violets appliqués à l'examen des couleurs et des agglutinants. - "Museum", 1933. V.21-22 N. 1-2, P. 32-68.

ABSTRACT

The recent restoration of five civic guard group portraits by Frans Hals (1581/85-1666) in the Frans Halsmuseum Haarlem, the Netherlands, is briefly described. In conjunction with the restoration a technical examination was carried out using mainly stereomicroscopy, X-radiography and paint sample analysis. A better insight into the painting technique was thus obtained. Discolouration of smalt, copper resinate green glazes and indigo influences the appearance of the paintings. Numerous modifications during painting were detected. Frans Hals made an essential use of his fairly light grounds.

KEYWORDS

Frans Hals, paintings, restoration, scientific examination.

ASPECTS OF THE RESTORATION AND TECHNICAL EXAMINATION OF THE HAARLEM CIVIC GUARD GROUP PORTRAITS BY FRANS HALS

Anne van Grevenstein, Karin Groen, J.R.J. van Asperen de Boer*, Liesbeth Abraham and Koos Levy-van Halm.

* Institute for Art History, History of Architecture and Archeology, Groningen University, Oude Kijk in 't Jatstraat 26, 9712 EK Groningen The Netherlands

1. Introduction

Five Haarlem civic guard group portraits are preserved which Frans Hals painted in commission. They are all in the Frans Halsmuseum, Haarlem. Three of these large format paintings, the Banquet of the Officers of the St George Civic Guard, c. 1616 (Cat. 123), the Banquet of the Officers of the St George Civic Guard, c. 1627 (Cat. 124) and the Banquet of the Officers of the St George Civic Guard, c. 1639 (Cat. 127) were painted for the building of that Guard. The two others, Banquet of the Officers of the St Hadrian Civic Guard, c. 1627 (Cat. 125) and the Officers and sergeants of the St Hadrian Civic Guard, 1633 (Cat. 126), decorated the main room of the Cluveniers Doelen. Cat. 123 is signed with a monogram 'FH F'. They have always remained in Haarlem but were transferred to the Town Hall in 1820 and to the actual Frans Halsmuseum in 1913. No contracts, designs or accounts have been preserved to throw light on the genesis of these paintings. Around 1740 four paintings were provided with numbers in white paint to facilitate the identification of the sitters. The earliest painting, Cat. 123, carries no such numbers.

The recent treatment of the five paintings - all having been relined in the past - was thought necessary for a number of reasons. There was poor attachment to the stretchers with numerous nails through both original and relining canvas causing deformations. Especially in Cat. 127, where nails were driven into the front of the stretcher bars, this had led to severe bulging of the painting in the lower zone. Puttied areas where the original canvasses were damaged showed up disturbingly. Serious cupping due to earlier treatment and yellow varnish impairing the readability and appreciation of colour values were important factors as well. Until recently there was a paucity of data on the painting materials and technique of Frans Hals paintings. De Wild (1) analysed some pigments but very little was published until the recent contribution by Groen and Hendriks (2).

A first examination of the five Haarlem paintings began in late 1981 aiming primarily at investigating the paint layer structure and composition (3). This included inspection with a stereomicroscope; 16 samples were taken by Van Asperen de Boer and prepared by Nelissen. Early in 1984 it was decided to restore the five paintings. In preparing a plan for this restoration Van Grevenstein solicited the collaboration of Groen who examined more paint samples, 14 taken by Van Asperen de Boer and Beate Federspiel and 23 by herself. Six additional samples were taken by Van Asperen de Boer during the restoration and prepared by Abraham.

X-radiographs were taken by Guido Van de Voorde of Brussels (4). More extensive examination with the stereomicroscope resulted in a preliminary report by Beate Federspiel.

An unpublished report was submitted to an Advisory Committee in January 1985. This Committee was established at the request of the Director of the Frans Halsmuseum.

Research in the Haarlem Archives was carried out by Levy to supplement existing data on the material history of the paintings.

The actual restoration supported by a grant from the Dutch Ministry of Culture began in early 1985 and was concluded by October 1987. A varying team under the direction of Anne van Grevenstein included Michaela Burek, Carol Pottasch, Amelia Jackson, Karin Tams, Beate Federspiel, Claudia Breuer-Castelli, Liesbeth Abraham and Ella Hendriks. Summaries of the material history and the restoration treatment of the paintings were included in a booklet aimed at a larger public issued in 1988 (5).

2. History of restoration

Before 1820 the five paintings were treated four to five times. The earliest payments for work on the paintings date from the end of the 17th century. In the early 19th century they were seriously damaged and repainted twice. From the 1860's on they became the nucleus of a municipal museum in Haarlem and were treated more frequently. Relining was carried out by an artist-painter. By the end of the 19th century the varnish was regenerated with alcohol vapour and copaiva balsam. This produced negative results and some public commotion as is evidenced by newspaper cuttings of 1908 and 1909.

An inquiry by the well-known restorer C.F.L. de Wild ensued in 1909. He concluded that only the varnish layer was damaged in these operations. Not until 1923 was a restoration project begun under the direction of D. de Wild. Except for Cat. 126 the paintings were not again relined. The restoration was limited to the removal of strongly yellowed varnish and the retouching of earlier repairs. Some laboratory analysis of pigments and varnishes was carried out. Elaborate reports have been preserved of this treatment intended to "last for centuries".

3. Treatment, cleaning and restoration

It was decided not to reline the paintings in view of the fair condition of the 19th century and 1923 interventions. It was understood that this would imply that the paintings could not be transported for exhibitions in the future. Most of the yellow varnish could be removed by gently rolling cotton swabs with acetone over the paint surface. This left intact an older non-analysed varnish of a probably oily nature - as it could be removed by slightly alkaline solvents - which gave the paint film a still saturated and slightly yellow appearance. As the preliminary investigation had shown a number of irreversible discolourations (cf. 4.2. below) it could be predicted that such alterations through ageing would become more visible and contrast between light and dark areas more pronounced by complete varnish removal. The knowledge that the paintings had been repeatedly subjected to the Pettenkofer regeneration process with the use of copaiva balsam - with well known plasticizing effects on paint layers - further incited to restraints in the cleaning procedure.

Large areas of overpaint such as the black glazes on all the garments, the brown glazing of the background of Cat. 126 and all the additions of the 1923 restoration were readily soluble in acetone. Older retouchings and lead white fillings were virtually impossible to remove by solvent action and had to be removed mechanically under the stereomicroscope.

The bulge in the canvas of Cat. 127 was reduced by removing the nails along the bottom edge and along c. 30 cm of the bottom side edges. These nails had been hammered through the original paint-layers and it was nearly impossible to remove them without some paint losses, however carefully this was done. The canvas was left to hang out in this manner for a couple of months and this was sufficient to reduce the bulge. The bottom edge of the old relining canvas could then be reattached to the stretcher.

After the application of an intermediate layer of dammar varnish, the lacunae were filled with a wax putty coloured in the tone of the ground; this varied from light pink to light brown. The surface structure of surrounding original paint was printed onto the surface of the filling with a mould of silicone rubber (type V 53 Romar-Voss, Roggel) using a heated spatula. The surface of the wax fillings was then isolated with a 30 % solution of Paraloid B 72 in acetone.

The reconstruction of the missing areas was made with the help of water colour copies by Wybrand Hendriks and Van der Vinne dating from the end of the 18th century i.e. before the extensive damage done to the paintings in the 19th century. These copies proved very useful in some cases where formal reconstruction was hypothetical. They also provided useful information about the original colour balance - at the end of the 18th century the copper resinate green hangings were apparently not yet discoloured.

A final layer of sprayed dammar varnish was applied to unify the surface without aiming at high gloss.

The paintings are shown after the restoration in their 18th century frames with the boards bearing names which correspond to the numbers painted on the individual portraits. These added numbers were not removed during the restoration but respected as being part of the historical entity of the paintings notwithstanding archival evidence that they cannot be by Hals' own hand.

Retouchings were carried out with dry pigments ground in dammar varnish. The reconstructions were made in the same medium chosen for its reversibility; they were first sketched out separately and discussed with advisors.

4. Scientific examination

4.1. Methods

Apart from the naked eye and ordinary photography the following methods were applied in the examination of the civic guard group portraits: raking light photography, ultraviolet fluorescence, X-radiography and infrared reflectography. Stereomicroscopy was used to assess further the condition and as a preliminary for taking paint samples. Macrophotographs were occasionally taken. Paint cross-sections obtained by embedding part of the sample in a clear polyester resin and subsequent grinding and polishing, were studied in dark field reflected light and ultraviolet fluorescence. Mounts were often made of blue and green pigments and these were studied in transmitted light and in crossed polars. In a few cases simple microchemical tests were applied to identify the pigments. Analysis of elements was systematically achieved by energy dispersive X-ray micro-analysis on the cross-sections prepared by Groen using an instrument at the Department of Earth Sciences, Cambridge. She also used infrared spectrophotometry to identify indigo.

4.2. Paint-layer structure and composition

Ground - All five paintings have a double ground. This consists of two light pink layers applied wet-in-wet containing lead white with umber and a little bright red ochre and black in Cat. 123. The top layer is a little darker and contains a little chalk. In Cat. 124 cross-sections show mostly only a single layer of light brownish-pink - sometimes two. The main pigment is again lead white with some chalk, umber, a dark red pigment and very little black.

A double ground of lead white with very little red ochre is found in Cat. 125; here the first ground is slightly darker due to admixture of fine black pigment.

Cat. 126 has a double brownish ground of lead white with dark brown umber and very little black; the lower layer is lighter. The double ground in Cat. 127 shows a translucent greyish first layer due to the presence of chalk as the main component; it further contains a little lumpy lead white, umber and a little yellow ochre. The second layer is opaque and brownish due to lead white, a little chalk, umber and a very little red ochre.

The grounds are all relatively light and allowed the artist to make use of their reflecting the incident light. In some areas it is the ground that shimmers through the paint and not some light underpainting. The lightish ground also influenced the technique of Frans Hals in painting flesh colours.

Blues - The skies and the sashes are virtually the only blues in the five painting. The sky in Cat. 123 is a layer of mostly discoloured smalt and lead white on a grey underpainting containing lead white and finely divided lampblack. A similar two-layer structure makes up the sky in Cat. 125. In Cat. 126 the sky consists of a single layer of smalt in lead white - hardly discoloured probably because less medium was used. A single paint-layer of discoloured smalt and lead white is found in Cat. 127.

The discolouration of smalt being an irreversible phenomenon (6) it seriously affects the colour balance in the paintings causing the bleak aspects of the trees and the dullish grey skies.

Indigo is the only blue pigment in the sashes. It was already found by De Wild (7) in Cat. 125, 126 and 127 using optical characteristics and microchemical behaviour. Groen has now identified indigo by infrared spectrophotometry in a sample of Cat. 126. Most sashes show a two- or three-layer structure with varying amounts of indigo and lead white. It would seem that an

extra layer was added when more hiding power was required locally to obtain the same overall tone; this is notably the case when the sash runs over a black garment so that the reflecting power of the light ground cannot be used.

The indigo used in the sashes seems to have faded - at least in the top layer. This is evidenced by the darker blue hidden beneath the frame of Cat. 126 but is difficult to appreciate from paint cross-sections. It is interesting to speculate about the rate of fading. Indigo has been used in underpainting from the 13th century on but its use as a pigment in the top layers seems very restricted indeed. It was not recommended in the 17th century (8). Could it be that the indigo faded during Frans Hals' lifetime?

Green - The greens of the foliage have badly darkened. In Cat. 123 and Cat. 125 it appears to be a mixture of azurite, ochre and bone black in a darkened matrix. In Cat. 126 the trees over the sky show azurite and lead white in a brown medium with a discoloured copper-containing glaze. In the foliage of Cat. 127 lead white, ochre and black are present. Discoloured smalt may have originally brought about the green colour. The curtain in Cat. 123 now looks brownish yellow except for a green strip at the left which was in an earlier stage covered by the frame. Paint cross-sections show that the yellow in the strip is covered by a light green layer and a dark green glaze both containing ground copper resinate. This apparently discoloured under the influence of light and oxygen and has been subsequently rubbed away during previous cleaning to a large extent. UV-protecting film has now been installed in the roof of the exhibition room and will hopefully prevent further deterioration in the now exposed strip.

Reds - Only a limited number of samples was taken in red areas. In Cat. 124 the red flag consists of a thin bright red layer of red ochre with red organic pigment and some bone black; the shadows are applied in a thick glaze of red organic pigment with some red ochre, bone black and lead white. The red flag is applied onto a grey underpainting of lead white, lampblack and very little ochre or umber.

A sample from a red sash shows two thick layers containing organic red pigment, red ochre and chalk on a yellow underpainting. The red sashes in Cat. 125 show a similar build-up.

A red cape in Cat. 125 consists of three layers with varying amounts of vermillion and red organic lake. A red sash in Cat. 126 shows two layers of bright red ochre with little lead white and in the lower layer some organic red.

Orange/yellows - A yellow coat in Cat. 124 consists of two layers on top of a greyish layer (lead white and lampblack). The lower layer is composed of brown ochre, bone black, some organic red pigment and lead white; the top layer of lead white with yellow and brown ochre. In Cat. 126 a yellow sash contains lead-tin yellow, lead white and chalk. An orange sash in Cat. 127 consists of vermillion with yellow ochre and lead white. There is thus no evidence for the use of orpiment or realgar.

Blacks - Only two samples were taken in the black dresses of Cat. 127. They consist of several layers but the thickest one contains large lumps of lead white in a black matrix. It seems obvious that such a grey layer would possess particular scattering characteristics which may account for the extraordinary transparency of Frans Hals' black garments.

4.3. Modifications and other aspects of painting technique

X-radiographs reveal quite a number of modifications. They are mostly related to the position of hands. Heads and aspects of the backgrounds. In some cases the modifications bear a relation to the change in status of the portrayed. This has been shown to be the case for one of the halberds in Cat. 127 (9).

X-radiographs also show clearly that Frans Hals used different amounts of lead white in painting flesh colours. Sometimes much use was made of the light ground and notably the faces thus have a different opacity. This is somewhat more visible after the recent cleaning. It is not clear how Frans Hals achieved a first sketchy outline on the light ground. Infrared reflectography of Cat. 124 has shown that a glass and two collars had different positions indicated in black paint.

5. References and notes

1. A.M. de Wild, The Scientific Examination of Pictures (London: G. Bell, 1929).
2. Karin Groen and Ella Hendriks, 'Frans Hals: a Technical Examination', in: Frans Hals, Exhibition Catalogue (S. Slive, Ed.) Washington 1989, London and Haarlem 1990, 109-127.
3. C.H.M.A. Nelissen, 'De schuttersstukken van Frans Hals in het Frans Halsmuseum te Haarlem', (unpublished minor thesis submitted to J.R.J. van Asperen de Boer, Groningen University 1984, 83 pp. including a survey of data on the material history).
4. Guido Van de Voorde, 'Het gebruik van de Cronaflex-film voor de radiografie van schilderijen', Bulletin Institut royal du Patrimoine artistique XIV (1973/74), 34-38.
5. Norbert Middelkoop and Anne van Grevenstein, Frans Hals - Life Work Restoration (Amsterdam: Uniepers, 1989), 112 pp. A videotape showing aspects of the restoration work was issued in 1988 by the Frans Halsmuseum.
6. J. Plesters, 'A preliminary note on the incidence of discolouration of smalt in oil media', Studies in Conservation 14 (1969), 62-74; R. Giovanoli and B. Mühlethaler, 'Investigation of discoloured smalt', Studies in Conservation 15 (1970), 37-44.
7. A.M. de Wild, op. cit. (note 1), 31.
8. J.A. van de Graaf, Het de Mayerne manuscript als bron voor de schildertechniek van de barok (Thesis Mijdsrecht: Drukkerij Verwey 1958), 44.
9. J. Levy-van Halm and L. Abraham, 'Frans Hals, Militiaman and Painter: the Civic Guard Portrait as an Historical Document', in: Frans Hals, Exhibition Catalogue (S. Slive Ed.) Washington 1989, London and Haarlem 1990, 87-102.

ABSTRACT

Methods of isolating organic components of paints in archaeological samples of painting and sculpture in Kara-tepe monuments have been worked out. Preliminary tests and the IRS-analysis made it possible to refer them to the class of polysaccharides. The identification of polysaccharides isolated from the paints was done by the paper and liquid chromatography technique. Fruit tree gums were used for comparison. In spite of the obvious resemblance in the chromatograms of the samples, certain differences were found in them, caused by different composition of the samples under investigation.

KEYWORDS

Spectrophotometry, Chromatography Methods, Infra-red spectra, Mono-, Oligo-, Polysaccharide, Binding of Paint.

ANALYSIS OF PAINTING BINDING MATERIALS CONTAINING POLYSACCHARIDES BY PHOTOMETRY METHODS AS WELL AS BY PAPER AND LIQUID COLUMN CHROMATOGRAPHY

V.N.Yarosh
VNIIR
10 Krestyanskaya Pl.
Moscow, USSR

Introduction

As is known, ancient masters, when making paints for painting, often used substances constituting hydrocarbons, or having hydrocarbon components in their composition. Instructions on paint-making methods using hydrocarbons are given in many ancient manuscripts and books. It is known, for instance, that cereal broths of wheat and rye were used long time ago for making paints based on blue pigments, and gum arabic solutions were used for erasing cinnabar. Miniatures on parchment were executed with paints based on gum or egg white solutions.

Consequently, detection and identification of polysaccharide components in the composition of paints is a very topical task.

In this paper we cite data on the application of spectrophotometry and chromatography methods for detection of polysaccharides in model and real samples of painting.

Analysis

In order to practice analysis methods of polysaccharide components in painting samples we made model samples based on flour glues, filled with chalk and without a filler. In addition, gums including gum arabic and gums of some species of fruit trees were prepared for the experiment. Glue films made of rice and oat grains, as well as of rye and wheat flour, potato starch and linseed broths were cast out of water solutions of these materials on glass and foil substrates. Part of the solutions were whipped up with chalk and the resulting suspension was also applied to substrates.

Models made in this way were first air dried, and then in a temperature - controlled cabinet with slight heating, and after that aged in natural air conditions for six months.

In order to detect hydrocarbons in the composition of paints the reaction of mono-, oligo- and polysaccharides with phenol and sulphuric acid, well-known in biochemistry, was tested /1/. This is rapid and reliable method of a qualitative and quantitative estimate of the presence of hydrocarbons in the samples. The reaction begins from hydrolysis of saccharides on to furfural which makes with phenol products of brown colour. The optical density of coloured solutions is measured at 490 nm /2/.

The reaction with phenol and sulphuric acid was first tried on samples of dextran. To do so, standard dextran solutions of different concentration were prepared; 1 ml of each solution was treated with 1 ml of 5 p.c. phenol solution and 5 ml of sulphuric acid were added to it. A reddish-brown colouring (Fig. 1) that appeared after a few minutes was recorded by the spectrophotometer.

The values of the optical density of dextran solutions colouring in water with the reagent phenol + sulphuric acid were as follows:

C, mg/ml	110	55	22	11
D _{490 nm}	1.26	.62	.29	.10

A calibration graph of the linear dependence of 'D' on 'C' was drawn. The content of polysaccharides in archeological samples of wall paintings of two monuments of Toprak-kaly and Kara-tepe in Soviet Central Asia was ascertained by means of this graph. These values for different samples of Toprak-kaly paintings constituted .03-.04 p.c., and for samples of Kara-tepe paintings, .02-.03 p.c. recalculated for dry substance.

Further, this reaction was made on samples of vegetable glues films (model samples), as well as on old paintings samples. The results are given in Table 1.

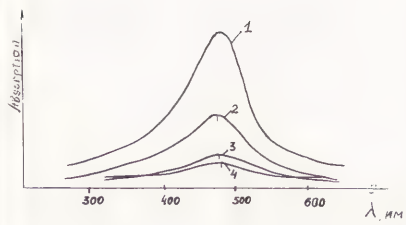


Fig.1 Adsorption spectra curves in the visible sector of various polysaccharide solutions after reaction with phenol and sulphuric acid of the following substances: 1-dextran, 2-the white of an egg, 3-the egg yolk, 4-doubling glue of the 17th century picture.

Table 1

Adsorption of Solutions of Painting Samples and Model Samples After Reaction with Phenol and Sulphuric Acid

Sample	Max nm	Microchemical protein test	Complex investigation result
Starch	488	-	
Rye glue	492	+	
Wheat glue	490	+	
Chalk + 1 p.c. wheat flour broth	495	+	
Linseed broth	480	-	
St.Sophia Cathedral, Kiev City, plaster under painting, Southern gallery	490	+	flour glue
Ground coat of decorated ceiling on canvas, Ilyinskaya Church, Byelozersk	490	+	cereal broth (rye, oats)
Doubling glue of 'Still Life' picture, 17th century, artist anonymous, Holland	490	+	flour glue
Glue from the sleeve of a military uniform, 19th century, State Museum of History	490	-	starch

The preliminary preparation of a sample included sample grinding and its extraction by water and water-alcohol solutions. For the purposes of a qualitative analysis, however, this reaction can be made also in water or water - alcohol suspension of a ground sample of painting containing inorganic components as well. As our experiment showed, mineral substances in paints have no adverse effect on the reaction process. The reaction is reliable for samples containing a sufficient quantity of neutral oligo- and polysaccharides. The reaction is best made in a wide test tube, and the acid poured not along the test tube walls, but into its centre for a more intensive heating of the solution and for acceleration of sugar hydrolysis.

Chromatography on Paper

In order to conduct chromatographic investigations, including paper and column chromatography, samples of gum and samples of painting were prepared. Gum arabic, cherry and plum gum and tragacanth were selected for the experiment. Gum hydrolysis was made in a hydrochloric acid solution at 110°C.

Mixtures of standard monosugars were prepared for chromatography: glucose, arabinose, ramnose, mannose, galactose, xylose and fructose, galacturonic and glucuronic acids. Chromatography was made on paper FN-11, eluation, with a mixture of pyridine - butanol and water 6:4:3, developing, by AgNO₃ solution and subsequent treatment with alkali and thiosulfate. As a result of the experiment, we succeeded in a good separation of monosugars and distinguishing hydrolysates of some gums by their composition. The values of R_f when separating some monosugars on paper are given below:

Names of sugars, R _f	Gum hydrolysates cherry, plum, traga- canth			Hydrolysate of painting binding sample from Kara- tepe wall
Glucuronic acid, .15	+	+	-	+
Galacturonic acid, .20	-	-	+	+
Galactose, .38	+	+	+	+
Glucose, .4	-	-	-	-
Mannose, .43	+	-	-	-
Arabinose, .45	-	+	+	+
Xylose, .50				
Ramnose, .55	+	-	-	-
Fructose, .48	-	-	+	-

When separating on paper hydrolysates of painting samples from Kara-tepe and Toprak-kaly monuments we detected weak spots relating to acid monosugars and several spots of neutral sugars, including galactose and arabinose (for the sample cited in the table), and also those of mannose, glucose and xylose for the other samples. Thus, proceeding from the results of paper chromatography one could suggest that the composition of painting binding materials of these monuments included polyurenides, i.e. acid polysugars contained also in the composition of some gums. Apart from chromatography on paper, liquid chromatography was carried out on columns with different carriers.

It is worth noting the way binding material was isolated from ancient painting samples. A paint layer, separated from the ground coat, was ground and treated in turn with diluted alkali and sulphuric acid solutions with weak heating. Combined solutions were neutralized, centrifuged and dialysed against water. Then the solutions were evaporated on a rotor evaporator, and the resulting products were lyophilized. The substance isolated yielded in different samples from .1 to .5 p.c. of the weight of the initial painting samples from the Kara-tepe monument. A recording was made of infrared spectra of substances isolated, which contained the principal adsorption bands of polysugars and were quite similar to the infra-red spectra of gums (Fig. 2).

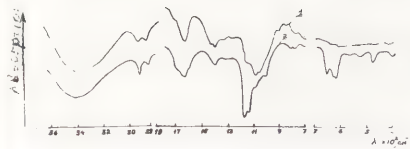


Fig.2 Infra-red spectra of the polysaccharide isolated from a paint sample of Complex 'B' Cave wall of Kara-tepe monument (curve1) and Arabian gum - gum arabic (curve 2)

Chromatographic separation was done on a column with Sefadex containing ion-exchange resin*. Chromatography conditions: eluation first by phosphate buffer then by phosphate buffer gradient and .5-1.0 NaCl solution, recording by the adsorption of coloured solutions formed by the reaction of products, outgoing from the column, with orcin and sulphuric acid solutions by Technicon analyzer.

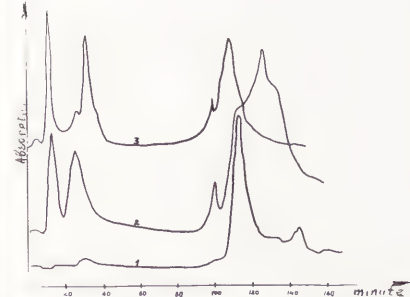


Fig.3Separation of polysaccharides on a column with sefadex treated with ion-exchange resin:1-chromatogram of a polysaccharide from the point of a palace in Toprak-kaly monument, 3-chromatogram of traga-canth

At about the 30th minute the column yielded products which may be characterized as neutral polysaccharides, they went practically without delay from the column. About 2 hours after the experiment began, and 1 hour after buffer gradient was introduced, two products were yielded, which may be related to acid polysaccharides (Fig. 3).

As can be seen from the chromatogram cited, the binding materials of wall paintings in Kara-tepe and Toprak-kaly have some features in common and some differences. Their similarity lies in that the two products have in their composition neutral and sour polysaccharides. The amount of neutral products in Toprak-kaly paints, however, is much greater than that in a paint sample from Kara-tepe. Besides, the composition of fractions, containing acid polysaccharides, is different in these samples. In the polysaccharides sample from Toprak-kaly paint there are more acid products than those isolated from Kara-tepe painting sample.

Apart from ion-exchange chromatography on Sefadex, separation of binding materials was done on a column with Fractogel** (Fig. 4).

* Sefadex QAE, A-25 (Pharmacia Fine Chemicals AB, Sweden) Anion exchanger, particle size 40-120 (Sweden).

** Fractogel TSK 40 (Merck).

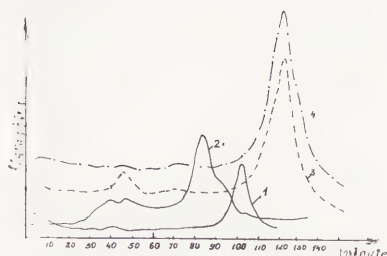


Fig.4 Separation of polysaccharides on a column with acrylic gel: 1-polysaccharide from the red paint of sculpture painting, Complex "D" Kara-tepe monument, 2-polysaccharide from the paint of a fragment of the wall painting of Complex "B" Kara-tepe monument, 3-polysaccharide from sweet cherry gum, 4-polysaccharide from cherry gum

The chromatograms obtained show that there are certain differences in the composition of binding materials of even one monument. For instance, chromatographic curves 1 and 2 (Fig. 4) differ. Curve 1 is the result of the column yielding a product isolated from the paint of Complex "D" Cave, and curve 2, of a product from the paint of Complex "B" Kara-tepe monument. For comparison, Fig. 4 shows chromatograms of polysaccharides of cherry and sweet cherry gums. Separation conditions: the filler is Fractogel**, elution by phosphate buffer and phosphate buffer gradient and NaCl solution.

In order to find out the composition of products isolated acid polysaccharides were first methylated, and then reduced to corresponding polysugars which were hydrolysed in 2 N HCl solution at 110°C. HCl was removed in vacuum, and hydrolysate was evaporated, and the mixture was analyzed to detect separate sugars by a special hydrocarbon analyzer (Biotronic, the FRG) on anionite*** in borate buffer. Among hydrolysis products we found such sugars as rhamnose, mannose, arabinose, galactose, xylose, glucose and some unidentified substances. Thus, compositions of binding materials isolated from paints turned out to be similar to gums, products of plant pathological development, although one cannot exclude that plant juices were added to paints, which contained the so-called pectin substances, polyureide which are present in many land plants.

Conclusions

1. Reaction with phenol and sulphuric acid has shown itself to advantage when identifying carbohydrates in painting samples. The technique proved to be express and reliable.
2. The identification of bindings of paints was done by the paper liquid chromatography techniques. The liquid chromatography technique on Sefadex, modified by the ion exchange resin, makes it possible to identify hydrolysis products of neutral and acid polysaccharides.
3. An analysis was made of bindings in archaeological samples of painting in Kara-tepe monuments in Central Asia.

Components relating to gums were found in the composition of bindings of paints.

Bibliography

1. Dubois M., Gilles K.A., Hamilton J.K., Rebers P.A., Smith F. Colorimetric method for Determination of Sugars and Related Substances, Analytical Chemistry, 1956, v. 28, N 3, p. 350-356.
2. 'Photometric Analysis' by N.I.Korenman. Moscow, Khimiya, 1975.

** Fractogel TSK 40 (Merck).

*** Durrum DA x 4 (Biotronic).

ABSTRACT

A computer program for processing the X-ray diffraction data has been established. The program can be used for saving the data, identifying the phases and comparing the studied samples with JCPDS standards. The results of this comparison are data sets of three coefficients ready for further statistical and mathematical treatment (e.g. cluster analysis).

KEY WORDS:

personal computer, mathematical evaluation, X-ray diffraction, cluster analysis, museum collections

THE APPLICATION OF IBM PERSONAL COMPUTERS (IBM PC) FOR MATHEMATICAL EVALUATION OF X-RAY DIFFRACTION DATA IN PRESERVATION AND SCIENTIFIC REASSESSMENT OF MUSEUM COLLECTIONS

Petr Zalabák^{x1}, Zdeněk Urbanec² and Jiří Čejka¹

1 National Museum in Prague, 115 79 Praha 1, Czechoslovakia

2 Nuclear Research Institute, 250 68 Řež, Czechoslovakia

Introduction

X-ray diffraction is one of the most important instrumental analytical methods to study various material presented in museum collections [1]. The method enables us to determine the phase composition of archaeological materials (pottery, bones, products of metal corrosion), mineral phases, pigments, plasters and mortars. It provides a considerable help in solving problems of preservation and conservation of collections and their scientific estimation. Systematically supplied files of standard diffraction data (Powder Diffraction File, JCPDS-ASTM) enable the treatment of experimental data not only in a visual way but also using the computers as well. The great deal of software is now at our disposal. Data treatment has been usually done using big computers. Therefore we have concentrated on the possibility of the data treatment with an IBM-PC compatible computer which can be placed in every laboratory.

An X-ray device which we used has an analog output. Therefore we do not deal with a communication between the X-ray device and the computer on line.

We start from the fact we need to treat large sets of samples because only the mathematical and statistical evaluation of such sets gives important information not only for preservation, conservation and restoration of these materials but also for their scientific estimation. The previous work was concentrated only on evaluation of the results of elemental analysis obtained by optical emission spectroscopy by using the cluster analysis [2].

2. Experimental data processing

2.1. Program for comparison of experimental data with JCPDS standards (RTGDIFR)

This program enables very easy data setting, their edition including correction and adding. The main function of this program is to compare experimental data with the JCPDS (Joint Committee on Powder Diffraction Standards) standards.

The application of the program is very simple, the dialog with the computer is realized by a system of menus and does not call for knowledge of programming.

2.1.1. Data organization

Experimental data for the program RTGDIFR are organized into the files according to the general subject. It is possible to work with individual samples or to process whole data files. Each sample contains name, note (any text) and the interplanar spacings (d-spacings) with the intensities of up to 40 most intensive lines. The data file is updated after escaping from the edit mode of each sample, so it is not necessary to save it into the disk. The size of the data file is limited only by disk capacity.

2.1.2. Data setting into the program

Standard version of the program RTGDIFR is ready to input the data directly from keyboard. After opening of the data file the access to all the samples from the file is possible by typing its name. Adding or deleting of any number of samples is possible.

The diffraction data are put in as diffraction angles (2θ) in degrees and peak intensities in cm. The data are recalculated immediately into the interplanar spacings according to a wavelength of the radiation used and into the relative intensity in comparison with the most intensive line in the sample.

2.1.3. The comparison with JCPDS standards

The comparison of experimental data with JCPDS standards is the most important part of the program RTGDIFR. Either the comparison of individual samples or the comparison of whole sets of samples is possible. An index of 20 compounds with three coefficients [3] is the result of that comparison. These 20 minerals are selected from a library of JCPDS standards according to their U coefficient which shows similarity of the sample spectrum to the spectrum of standard. Following similarity coefficients are calculated during the process of comparison:

^x Author to whom correspondence should be addressed

Q coefficient - the number of standard lines that are in the interval in which was the sample measured

T coefficient - the number of lines of the sample situated in the tolerance interval of some standard lines

U coefficient - calculated according to the following formula:

$$U = \frac{\sum I_v^2}{\sum I_v^2 \cdot \sum I_s^2} \cdot \frac{T}{Q}$$

where I_v is the intensity of line of the sample,

I_s is the intensity of standard line

T and Q are coefficients presented above

The tolerance interval depends on a diffraction angle. That interval is calculated according to the following formula:

$$ti = c \cdot \frac{\lambda}{2 \cdot \tan \theta \cdot \sin \theta}$$

where λ is the wavelength of the radiation used

θ is the diffraction angle

C is an empirical coefficient the value which is 0.00625

This formula is the first-order derivative of Bragg's equation:

$$\lambda = 2d \sin \theta$$

$$d = \frac{\lambda}{2 \sin \theta}$$

$$\frac{dd}{d\theta} = \frac{\lambda}{2} \cdot \frac{\cos \theta}{\sin^2 \theta}$$

The value of the empirical coefficient in the formula for calculating the tolerance interval was determined from our experimental data.

The most important coefficient (U) expresses the value of similarity of both the spectra compared but not the content of specific phase in the sample, in case of the phase analysis. If its value is greater than 0.35, it is possible to expect the presence of the phase in the sample. If the value of U coefficient is lower, there exist some coincidences, probably. In case of the absolute correspondence of the spectra (both the intensities and the interplanar spacings), its value is 1.00.

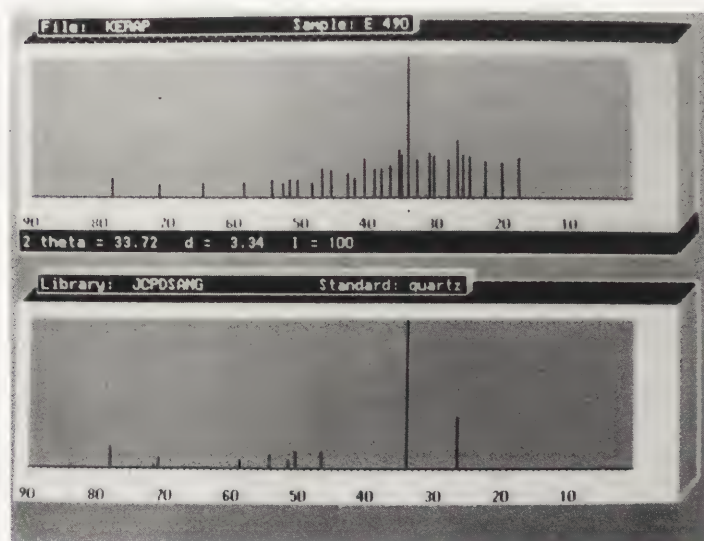


Fig. 1. Visual comparison of the sample spectrum and the standard one on the computer screen

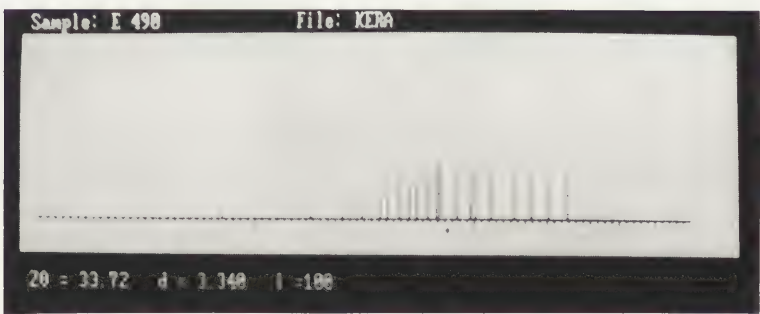


Fig. 2. The spectrum of the sample after subtraction of the standard spectrum

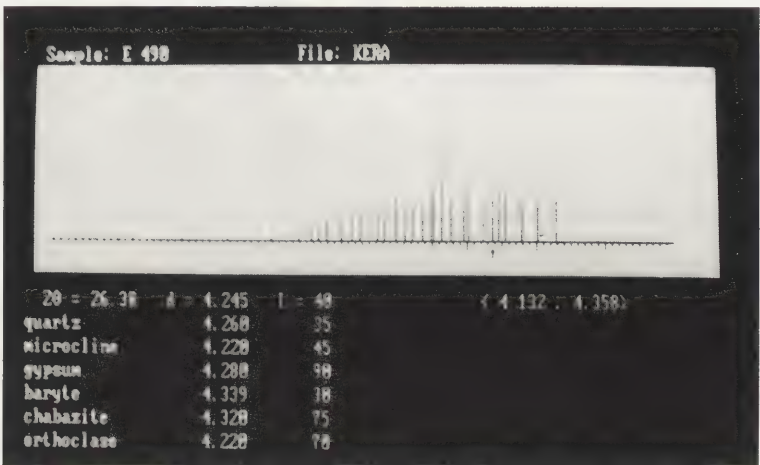


Fig. 3. The result of searching for isolated line of the sample spectrum ($d = 4.245 \text{ \AA}$) in the standard library

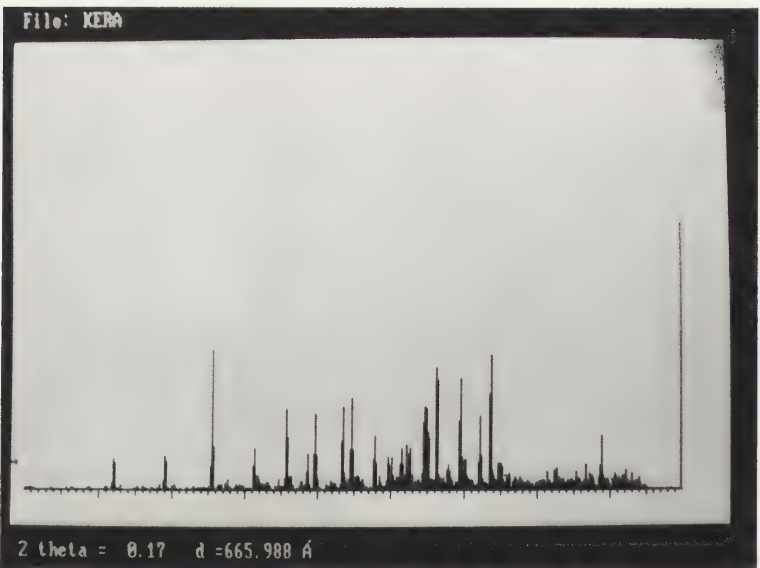


Fig. 4. The statistical spectrum of the whole data set of Egyptian pottery

The visual comparison of the sample spectrum with the standard one is possible, too (see figs. 1-3).

2.2. Possibilities of further statistical treatment

In case of the full utilization of reached data, it is recommended to treat them by some of the methods of one-dimension (see fig. 4) or multivariation statistical analysis (see fig. 5). Cluster analysis is mostly used to deal with the data [2].

The cluster analysis connects samples of most similar measured properties which can be of qualitative or quantitative character, too. The criteria of similarity may be chosen as follows: Sokal-Michener coef. and others, Euclid

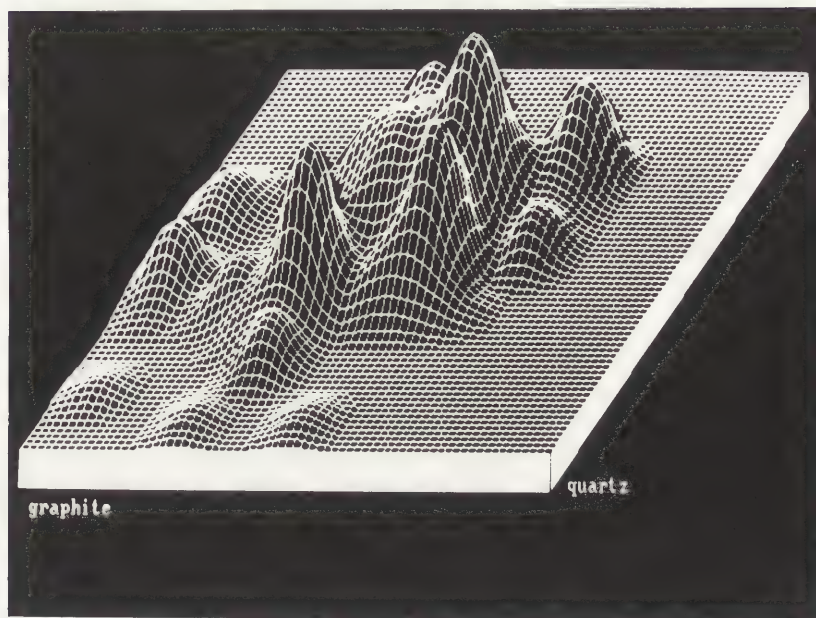


Fig. 5. Frequency surface of U coefficient values for quartz and graphite as a result of comparison the data set with JCPDS standards

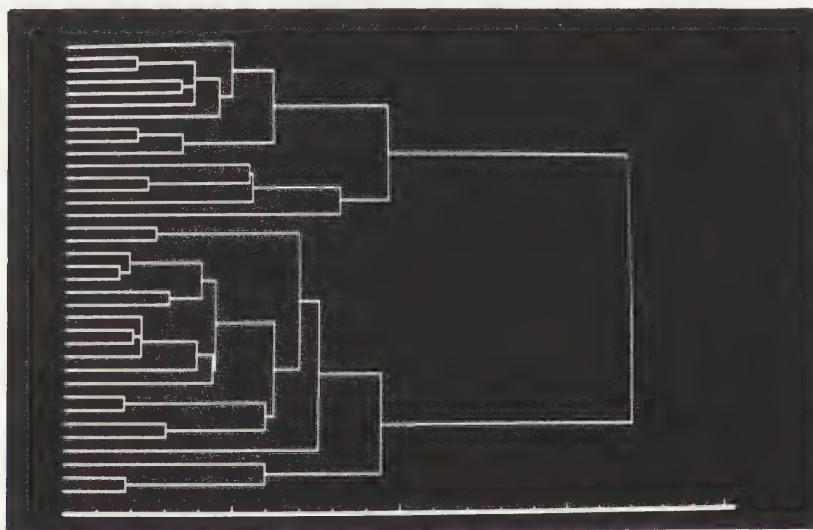


Fig. 6. The result of cluster analysis (version Q)

and other distances. The way of the treatment may be average linkage, single linkage and so on.

The cluster analysis results e.g. in dendrograms where levels of similarity of clustered samples by visual way can be observed (see fig. 6).

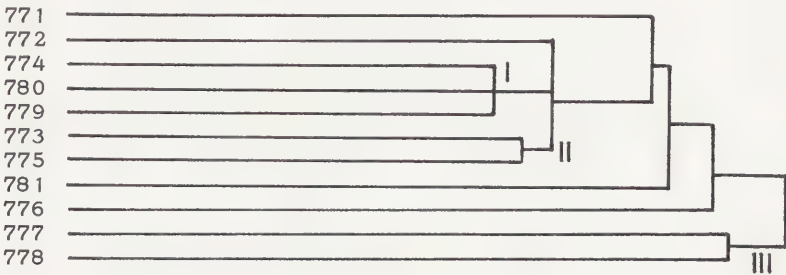
3. Example of application

The set of samples of ancient ceramics from some localities in South Moravia (Konůvky, Loštice, Žadlovce) is given as example of application. The first table shows experimental X-ray diffraction data of one of the samples:

List of lines		Sample: 781		File: BRNOKERA
Number	2 theta [°]	Intensity [cm]	d [Å]	Rel. intensity
1	11.20	21.30	9.926	98
2	12.80	15.30	8.690	71
3	14.15	15.00	7.864	69
4	22.45	9.90	4.976	46
5	24.75	6.90	4.520	32
6	26.35	8.55	4.250	39
7	27.90	5.95	4.018	27
8	30.45	18.35	3.688	85
9	33.70	21.70	3.342	100
10	34.90	13.30	3.230	61

Number	2 theta [°]	Intensity [cm]	d [Å]	Rel. intensity
11	37.90	5.75	2.983	27
12	43.65	3.95	2.605	18
13	46.50	3.45	2.454	16
14	47.85	2.70	2.388	12
15	50.30	2.70	2.279	12
16	54.10	2.95	2.130	14
17	58.15	4.20	1.993	19
18	64.40	3.10	1.818	14
19	70.55	21.70	1.677	100
20	77.90	2.15	1.541	10
21	88.95	0.90	1.383	4
22	89.75	0.95	1.373	4

The next diagram presents an application of cluster analysis on whole data set which contains 11 samples:



Groups I, II and III are discussed hereafter in the following table, samples 771, 772, 776 and 781 are not consistent with any group.

sample	771	772	774	I 779	780
quartz	0.721	0.632	0.481	0.534	0.329
graphite	0.660	0.344	0.358	0.448	0.439
cristoballite	0.404	0.000	0.194	0.348	0.000
spinel	0.399	0.228	0.000	0.000	0.000
wollastonite	0.396	0.405	0.216	0.248	0.278
biotite	0.364	0.389	0.277	0.247	0.240
illite	0.360	0.254	0.299	0.427	0.270
diopside	0.350	0.525	0.245	0.322	0.000
mullite	0.341	0.435	0.000	0.370	0.125
muscovite	0.324	0.000	0.140	0.300	0.000
albite	0.321	0.387	0.210	0.433	0.210
orthoclase	0.308	0.362	0.185	0.270	0.218
andalusite	0.303	0.249	0.167	0.000	0.134
augite	0.277	0.291	0.000	0.293	0.000
gehlenite	0.000	0.368	0.143	0.360	0.283
analcime	0.000	0.363	0.000	0.000	0.111
gypsum	0.000	0.262	0.000	0.320	0.233
hematite	0.000	0.231	0.252	0.182	0.332
hornblende	0.000	0.000	0.000	0.000	0.000
chabasite	0.000	0.000	0.216	0.220	0.000
baryte	0.000	0.000	0.143	0.000	0.128
anortite	0.000	0.000	0.164	0.000	0.141
anhydrite	0.000	0.000	0.000	0.000	0.125

sample	II 773	775	776	III 777	778
quartz	0.594	0.527	0.305	0.359	0.351
graphite	0.447	0.638	0.309	0.331	0.487
cristoballite	0.000	0.000	0.000	0.541	0.434
spinel	0.465	0.398	0.552	0.356	0.338
wollastonite	0.000	0.364	0.000	0.317	0.000
biotite	0.315	0.530	0.350	0.509	0.513
illite	0.286	0.297	0.423	0.000	0.000
diopside	0.572	0.481	0.656	0.453	0.477
mullite	0.515	0.400	0.452	0.889	0.933
muscovite	0.261	0.422	0.260	0.000	0.000
albite	0.396	0.000	0.428	0.000	0.000
orthoclase	0.395	0.458	0.405	0.353	0.336
andalusite	0.306	0.309	0.252	0.000	0.000
augite	0.498	0.295	0.497	0.364	0.502
gehlenite	0.369	0.293	0.479	0.000	0.000
analcime	0.000	0.000	0.303	0.412	0.404

sample	II		776	III	
	773	775		777	778
gypsum	0.349	0.340	0.000	0.396	0.423
hematite	0.344	0.279	0.000	0.346	0.422
hornblende	0.353	0.000	0.000	0.295	0.344
chabasite	0.326	0.371	0.301	0.351	0.000
baryte	0.321	0.265	0.000	0.359	0.000
anortite	0.000	0.262	0.384	0.000	0.375
anhydrite	0.000	0.000	0.000	0.312	0.328

sample	781
quartz	0.443
graphite	0.658
cristoballite	0.347
spinel	0.000
wollastonite	0.000
biotite	0.476
illite	0.466
diopside	0.272
mullite	0.247
muscovite	0.537
albite	0.411
orthoclase	0.461
andalusite	0.383
augite	0.317
gehlenite	0.228
analcime	0.000
gypsum	0.000
hematite	0.000
hornblende	0.265
chabasite	0.000
baryte	0.000
anortite	0.316
anhydrite	0.000

This table presents the U coefficients of each pottery samples as a result of comparison with JCPDS standards. Distribution into groups marked as I, II and III is evident from cluster analysis (see the figure above). Group I is characterized only by greater U coefficient for quartz. The samples clustered in the second group (II) have high U coefficients for quartz, graphite, diopside and mullite. The last group (III) has high U coefficients for mullite, biotite, analcime and diopside.

4. Conclusion

In this paper, the experience with the PC-computer in connection of experimental X-ray diffraction data and statistical evaluation using cluster analysis has been presented with regard to the application in museum chemistry, preservation and conservation of museum objects.

5. References:

1. Ch. Lahanier, "The powder diffraction pattern applied to the knowledge of works of art", *Chemica Scripta* 26A (1986): 47-55.
2. J. Čejka and Z. Urbanec, "Cluster analysis and its application in museum chemistry and conservation" (Paper delivered at the Sixth Triennial Meeting of the International Council of Museums Committee for Conservation, Ottawa, September 9, 1981), Report 81/1/4, 8 pp.
3. J. Fiala and J. Fialová, "Počítačový systém pro identifikaci fázového složení pomocí rentgenové difrakce" (A computerized X-ray powder diffraction identification system), *Chemické listy* 79 (1985): 48-57.

Working Group 2

Structural Restoration of Paintings
on Canvas

Restauration structurale des peintures
sur toile



ABSTRACT

Modulus of Elasticity (E) measurements have shown that stiff surfaces attached to softer substrates deteriorate rapidly in response to cyclical changes in temperature and relative humidity. Conversely, a softer outer layer firmly attached to a stiff substrate withstands environmental influences better, as expressed by the old painters' rule of "Fat Over Lean". In canvas paintings, this relationship becomes reversed during the aging process. With aging, the imbalance between the hardening paint layer and the concurrent loss of tension and stiffness in the canvas keeps growing. This imbalance makes reinforcement to stiffen the canvas inevitable, to properly preserve the image of the painting. Protective lining might be preferable to progressive damage resulting from neglect, or to treatments which have no effect on the main causes of deterioration.

KEYWORDS

Modulus of Elasticity, canvas paintings, stiffness, sizing, lining, environment, cracks, blisters, stress.

CHANGES IN RESISTANCE OF CANVAS TO DEFORMATION AND CRACKING (MODULUS OF ELASTICITY "E") AS CAUSED BY SIZING AND LINING

Gustav A. Berger
Director of Research
Art Conservation Research Foundation, Ltd.
115 West 73rd Street
New York, N.Y. 10023-2940, U.S.A.

William H. Russell,
Assistant Professor,
Georgia Institute of Technology
College of Architecture
Atlanta, Georgia 30332

The Rule of "Fat Over Lean"

The outer surface of every solid body expands and contracts with changes in environmental conditions. If a solid body is stiffer than the surface which covers it, then the softer, pliant outer surface is held firmly in place during environmental changes. The surface layer becomes thicker with expansion and thinner with contraction. However, its lateral expansions and contractions are restrained by its adhesion to the rigid substrate (support). Thus, the surface is constrained to absorb the forces by its own contractions or expansions, without creating any lateral movements.

The opposite takes place when a stiff and brittle surface is attached to a soft substrate. In this case, the expansions and contractions of the outer layer are no longer absorbed by its attachment to the substrate. A lateral shear-force is created which must be restrained by the adjacent parts of the surface. However, no surface is perfectly uniform. For example, the application of paint is heavier, dryer or softer in some parts of the surface than in others. External damages, such as impact or scratches, cause further irregularities in the surface and create weaker spots. These weakened areas have to withstand the same stress as the surrounding material of larger cross-section and greater stiffness. As a result, the stress concentrates on the weaker areas. As stress develops due to fluctuations in environmental conditions the material is deformed at these points of stress concentrations.

Protecting hard surfaces with a softer coating, such as paint, has become a common engineering practice. The use of paint for this purpose goes back hundreds if not thousands of years. It is expressed by the old painters' rule of 'Fat Over Lean'. This rule can be extended to all surfaces capable of resisting the influence of environmental changes: a fat (that is a soft) outer surface which is firmly attached to a lean (that is a stiffer) substrate, is capable of withstanding environmental changes and even mechanical damage for a long time. Failure to follow this rule can insure disaster for any material, be it paintings, stone monuments, tiles, or road pavements.

In the case of paintings, in particular, the paint cracks in response to environmental changes if a harder layer is superimposed on a softer (fatter) one. It also cracks, if the top layer of a painting becomes harder upon drying than the supporting layers. Specifically, if the support is weaker or softer than the paint film which covers it, the paint layer cracks and detaches.

Modulus of Elasticity "E"

The relative softness or hardness of materials attached to each other is of the utmost importance for the effectiveness of coatings, adhesives, and other conservation materials and treatments. Although this is commonly known, this relationship is often overlooked. Therefore, we have devised methods to measure and compare the stiffness of the materials used in canvas paintings. In these measurements, which are now routinely performed whenever we investigate a new material, we have tried to achieve the following:

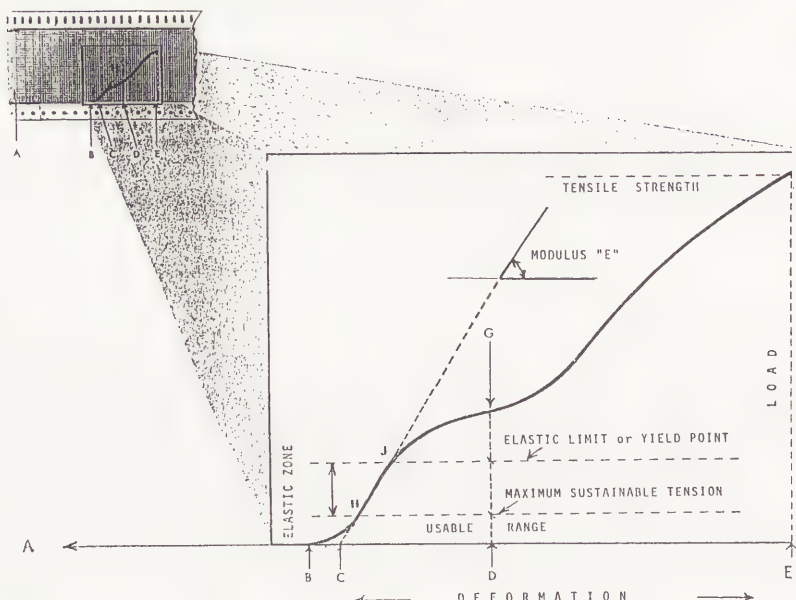
1. determine the resistance of canvas to displacement,
2. establish to what extent the stiffness changes under the influence of fluctuations in temperature and RH,
3. determine how tension, sizing, lining, and other conservation treatments influence the stiffness of the fabric, and
4. determine how the stiffness of old paint compares to the stiffness of old canvas (1).

Fig.1 Load-Deformation for Fabric from a Tensile Tester Chart

- Point A = Starting Point
 Line AB = Length of "crimp" in fabric
 Line AC = Deformation of straightened fabric at estimated zero elongation
 Line CD = Any specific elongation of fabric
 Line CE = Elongation at breaking point
 Line CJ = Line along the initial "straight line" portion of load-deformation curve BGF
 Line DG = Load required to elongate by the amount CD
 Point F = Breaking point of fabric (Tensile strength)
 Line EF = Breaking load
 Point H = Start of elastic zone and maximum stiffness (resistance to deformation)
 Point J = Elastic limit or yield point
 Line HJ = Slope of HJ gives the greatest Modulus E (maximum resistance to deformation)

Inclination (slope) of curve is proportional to Modulus E

(Adapted from "Stress/Strain Properties of Fibers", DuPont Technical Information Bulletin, 1958)



The force necessary to produce a particular deformation in a material is a measure of its stiffness, or resistance to deformation. This is normally expressed as Young's Modulus of Elasticity (E) which is defined, mathematically, as stress divided by strain:

$$E = \frac{\text{stress}}{\text{strain}} = \frac{\delta}{\epsilon} = \frac{\delta}{\Delta L / L}$$

where " δ " represents the stress increase causing the displacement, " ΔL " is the increase or decrease in length caused by the stress increase, and " L " is the original length of the object undergoing dimensional change. One can see that in order to find the modulus of stiffness "E", it is necessary to measure the increase (δ) required to change the size of an object, as well as the proportional change in size of the object ($\Delta L/L$) under the influence of this stress (δ).

Tension in Canvas and Modulus of Elasticity "E"

In an ideal linear elastic material, the Modulus of Elasticity is constant i.e. stress is directly proportional to strain (spring balance). Fabrics, however, are not ideal linear elastic materials and the Modulus varies with the level of stress. An unstretched, loose fabric has little resistance to deformation, and a stretched fabric loses its resistance to deformation as soon as it loses its tension. The tension in a stretched fabric fluctuates considerably with changes in RH. Additionally, soon after stretching, the tension begins to drop, and continues to do so even after frequent restretching (it usually drops by one third within two days) (2). After a few more days, in response to the fluctuations in RH, the tension drops to between 100-250 N/m depending on the weight of the fabric. We call this value the Maximum Sustainable Tension (MST in short) (3). There the stress remains fairly stable, except for the drastic changes which occur near 100% RH. The MST represents the upper limit of the usable range of tension of a canvas painting, and it is much lower than the values commonly used in industry for the capacity or strength of fabrics.

The diagram from a publication by DuPont from tensile tests on textiles (see fig.1) shows the usable range, at the bottom of the graph, to be only 5% of the total tensile or tear strength of the fabric. The upper limit of this usable range is at the lower portion of the linear elastic zone of the canvas. The modulus of elasticity (E) is proportional to the slope of this load-deformation curve. The diagram shows clearly that canvas reaches the highest attainable resistance "E" only when stretched

Fig.2 Changes in Tension in Tension in a "Shrinking" Canvas.

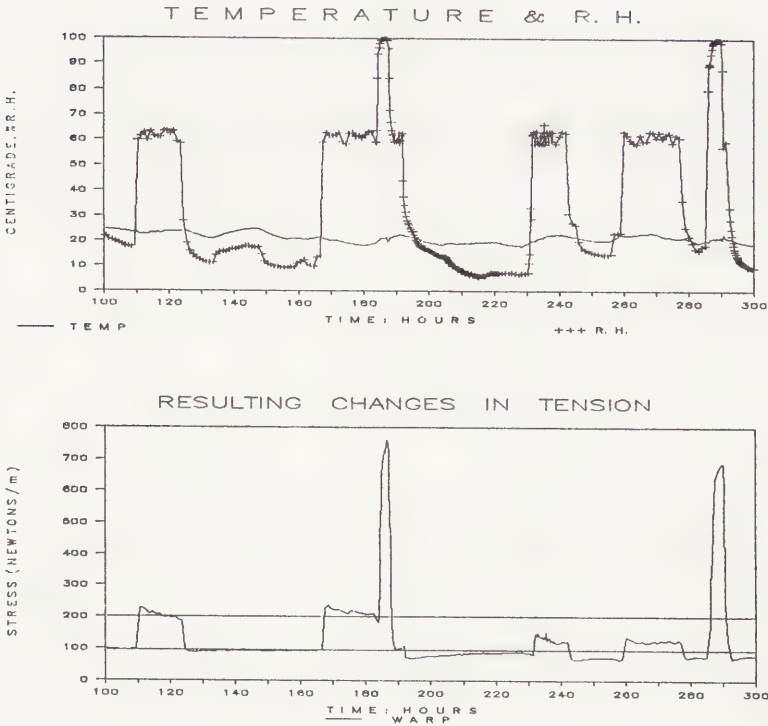
The horizontal axis shows the hours of the test, in this case, between 100 and 300.

2a Changes in Temperature and RH.

The RH is cycled between 10% and 60%, with an occasional rise to 100%, the temperature remains fairly constant between 22-25°C.

2b Changes in Tension caused by the environmental conditions in 2a.

Note the enormous increase in tension when the RH rises above 60%.



to the top limit of its usable range. Below this range, the stiffness "E" of the canvas drops rapidly. This can be seen by the flattening out of the slope of the curve, below and to the left of point "H". Between point H, and point J, the Modulus (E) is constant and the curve assumes a straight line. Therefore, any increase of tension above point H, no longer produces any increase in the Modulus (E), that is in the resistance of the canvas to deformation. Additional stretching of the canvas above point H, is in fact counterproductive, since it increases the long-term deformation or creep of the canvas.

Creep

Maintaining the fabric at the bottom of the linear zone is easier in principle than in practice. The tension in a raw, unsized canvas, changes with every change in RH (See fig.2). For example, a canvas which at 20% RH has a satisfactory tension of 100 N/m, might have double this tension at 50% RH, and at 100% RH its tension increases by 10 times. However, at this high tension, the canvas is overstretched. It becomes larger due to creep with a simultaneous relaxation in tension.

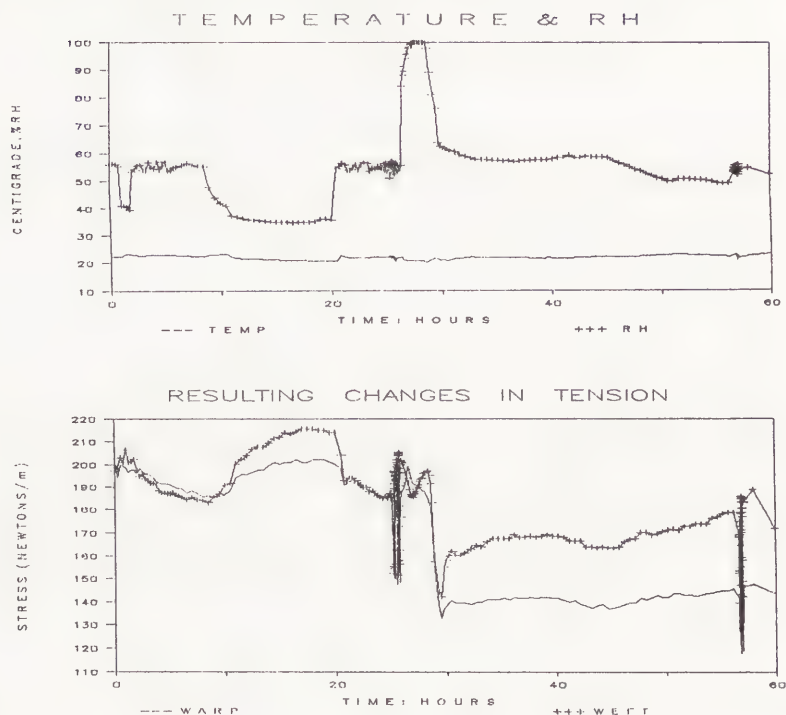
A mathematical expression for creep has been calculated by Andrade and verified by Conti and Tassinari (4). Their formula shows that the creep increases with tension cubed. Accordingly, if the stress doubles from 100 N/m to 200 N/m at the change from 20% to 50% RH, the creep increases eight times (2^3). Even more detrimental is the tenfold increase in tension at 100% RH which increases the creep 1000 (or 10^3) times the creep at 'normal' tension. Clearly, this enormous creep leads to a considerable elongation of the canvas with the resultant loss of initial tension. In addition, the creep factor also increases with the RH exceeding 60%. For example, Tassinari calculated that the creep of a canvas stretched to a tension of 4 Kg (400 N/m) at 80% RH is 1000 times larger than the creep of a canvas stretched only to 1 Kg of tension (100 N/m) at 40% RH (4). At 100% RH the tg of cellulose (i.e. the point at which plastic deformation occurs) is at room temperature, and the overstretched canvas suffers considerable elongation. Upon return to "normal" conditions, the canvas loses much of its original tension. This can be seen in fig.2a, where a short rise to 100% RH between the 185th and 186th hours causes a loss of tension of about 30%. The canvas has lost its tension because of the elongation it suffered under high RH. Once the canvas has lost this initial tension due to creep under high RH, it has also lost most of its stiffness (resistance to deformation). Thus, to preserve the stiffness "E" of the canvas it is essential to preserve the tension in the canvas when it elongates with a drop

Fig.3 Changes in Tension in an Old Painting.

A lightweight canvas (weight: canvas and priming 380 g/m^2) heavily painted in oil (weight of the paint ca $2000\text{--}2200 \text{ g/m}^2$), around 1930.

- 3a Cycling of RH between 40-60% with one rise to 100% and two short exposures to incandescent light (at the 26th and 58th hours of the test).
- 3b The resulting changes in tension. The big changes in tension at the 26th and 58th hours are caused by exposure to a spot-light. They exceed all the effects of changes in RH. The exposure to 100% RH causes little stress change because the stiff paint prevents shrinkage of the canvas. However, the canvas becomes over-stretched and, when the humidity drops in the 30th hour, it has lost a considerable amount of tension.

The large change in tension which registers as two heavy dark lines, are in effect several (3-5) severe fluctuations of 2-minutes duration each that merged because of the small scale.



in RH. It is equally important to prevent stress peaks at high levels of RH which lead to creep of the canvas. In general, to preserve the stiffness "E" in the canvas, it is essential to constantly maintain the lowest level of tension which still produces maximum resistance to deformation. This can be achieved by the following:

1. keep the environment, and particularly RH, constant to avoid changes in tension. This is an ideal situation rather than a practical solution.
2. create either complete micro-climates (which are often visually objectionable), or partial micro-climates, such as covering the back of the painting with cardboard.
3. use the self-adjusting, constant-tension stretcher. In numerous tests and implementation by leading museums, this stretcher has repeatedly shown a capability to absorb the most violent dimensional changes without significant stress increases. Conventional stretchers would cause a detrimental change of tension of up to 10 times under similar conditions (see fig.2), as described in previous papers (3 and 5).
4. increase the stiffness of the canvas and reduce its stress changes through sizing.
5. increase the stiffness of the canvas by lining or mounting on an additional support. The latter operation is performed using adhesives which often size the canvas in the process, thus adding to the effects of the lining treatment. They also reduce the effects of environmental fluctuations by protecting the reverse of the canvas.

Effects of Changes in the Stiffness of Paint and Canvas

All of the above treatments can be used either separately or jointly to preserve or increase the stiffness of the canvas. With aging, however, most fabric supports become weaker and more brittle while the stiffness "E" of the paint increases. This fact limits considerably the treatments available to the conservator. Eventually, the lateral forces generated by the stiffer paint exceed the resistance of the weaker canvas (see fig.3). The first cracks on a painting occur in the heavy layers of stiff paint, usually lead white. As this heavy paint ages, its stiffness rises. It becomes capable of generating sufficient lateral forces to overcome the resistance of the canvas to deformation, and of creating lateral movements within the paint layer. These lateral movements activate the "deformation traps" described in other reports by the authors (3, 5). The deformation traps lead to accumulations of dimensional changes which eventually generate sufficient stress to cause rupture and deformation of the paint film (see fig.4). With time and increasing paint stiffness additional cracks form and original cracks enlarge. The canvas conforms to the deformations

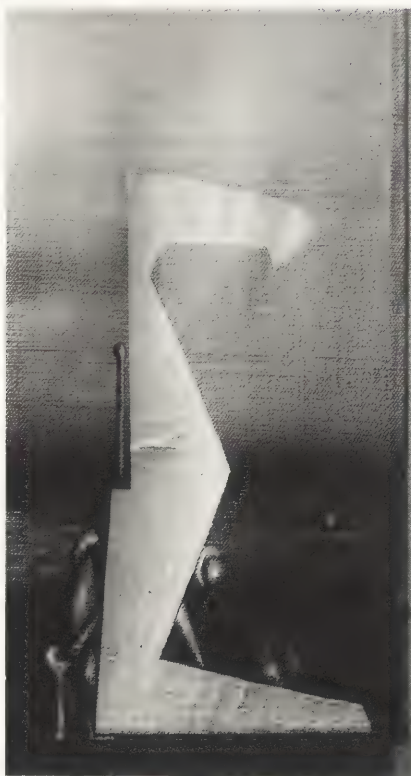


Fig.4 Yves Tanguy, "June Lune", oil on canvas, 28 x 25cm (Detail)

The canvas is loose, particularly in the horizontal direction which has the greater number of cracks. It is obvious that the paint film distorted the canvas since the canvas is loose in the area surrounding the heavily painted part. In addition, the distance between the cracks in the horizontal direction and those in the vertical direction is clearly different. This was shown to be due to the unequal resistance of the canvas to deformation (Modulus "E") in the warp and weft directions.

Note that the strongest cracks bisect the longest expanse of unbroken paint.

of the paint, as can be seen on the reverse of cracked paintings. It is, therefore, the paint film which creates these forces, rather than the canvas.

These forces have also been measured in our laboratory. Small changes in temperature produced by short irradiation with incandescent bulbs and reflectors produced large and abrupt changes in tension in samples taken from a 50-year-old heavily painted canvas (see fig.3). These observations contradict previous explanations which attribute cracking of paint films to the expansions and contractions of the canvas. Canvas can exert forces only when it is under tension, and when under tension, a canvas must be flat. Consequently, a bent, distorted, or flabby canvas is incapable of exerting any stress on the paint it carries.

Conclusions

In previous papers, the authors have attributed deformation and stress in canvas paintings to certain spatial configurations which they called "deformation traps" (3, 5). These "deformation traps" produce progressive accumulations of small plastic deformations in response to environmental changes. The accumulated deformations are not reversible, and lead to cracking, blistering, and cupping. The "deformation traps" can only be formed if the outer surface is harder than its supporting layer, or if it is not firmly adhered to it. This permits lateral movements in the surface with resulting stress concentrations in the places where these movements are interrupted by defects in the paint film or discontinuities in its design. In addition, the effect of the deformation traps might be aggravated by the stiffening of the paint media through drying and cross-linking. Whatever the cause, their effect must increase with aging, unless steps are taken to counteract them. This damage inexorably leads to the destruction of the structural integrity of the painting and the legibility of its visual image. For this reason, the eventual reinforcements of the canvas becomes inevitable. The timing of corrective measures is important. Once these forces have succeeded in cracking and distorting the paint film, they become much more difficult to treat without causing damage to the texture of the painting.

A painting has been described as a visual illusion created in a plane. The more refined or subtle an image, the more disturbed it becomes by any distortion of its "plane of reference". Thus, a minimalist painting, such as one by Reinhardt or Rothko, can become "illegible" with the slightest disruption of its surface. The preservation of this "plane of reference" and the image it carries should, therefore, be the first priority and concern of the conservator of paintings.

Ample proof is provided by paintings on a stiff support, and particularly canvas paintings lined with a stiff support, which are well preserved as compared to those left without reinforcement (3,5). Conservators should carefully weigh the proven and well documented protection which a good lining provides. Since 1972 numerous reports have been published showing that it is possible to line paintings without damaging their surface and appearance (6,7). At the Greenwich Symposium on Lining Techniques (1974), a dried butterfly was mounted with Beva(R)371 during a public demonstration to prove the above statements (8) (See fig.5).

Recent advances in research on sizing have also shown more effective ways of reinforcing canvas. However, any new approach to the preservation of paintings without lining must address the following causes of deterioration of canvas and paint:

1. The canvas progressively loses strength and stiffness with age.
2. The paint inevitably increases in stiffness with age.
3. The susceptibility of both, canvas and paint, to damage by environmental changes results from the increasing imbalance between the relative strength and stiffness of canvas and paint.

Acknowledgements

The authors wish to thank the Samuel H. Kress Foundation and its President, Dr. Marilyn Perry, for their financial and moral support of this research project since its inception.

Grateful acknowledgement goes to the Georgia Institute of Technology College of Architecture.

To all the other dedicated friends and supporters, gratitude is expressed.

Fig.5 "The Guitar"- A freshly painted collage, 60x40cm, following 'Vacuum Lining Without a Membrane'.

This collage, containing a dried butterfly, guitar strings, and high impasto, was prepared for the International Symposium on Lining in the National Maritime Museum in Greenwich, England (April 1974). It was lined in a public demonstration on a standard vacuum hot table, using several coats of BEVA 371 to make the reverse of the collage air-tight and to achieve suction. No pressure was applied to the face of the collage, and no part of it was damaged in any way.



Materials

8. BEVA^(R). The exact formula of BEVA 371 was first published in the Preprints to the 5th IIC Congress in Lisbon (1972), 613-628, and thereafter twice in *Studies*, twice in *Maltechnik/Restauro*, and in professional magazines in the USA. BEVA products are available from the following authorized sources:

1. Conservator's Products Company, P.O.Box 411, Chatham, N.J. 07928, USA. Tel. (201) 927-4855,
2. Conservator's Products Company of Canada, 23 Morrow Ave., Toronto, Ont. M5R 2H9, Canada, Tel. (416) 539-8069,
3. Archival Aids, Ltd., P.O. Box 5, Spondon, Derby, DE2 7BP, UK, Tel. (0332)-666400,
4. Ing. Dal Monte, CTS SAS, Via Piave, 36077 Altavilla Vicentina (Vicenza), Italy, Tel. 444/521310.

Notes and References

1. G. Hedley, "The Stiffness of Lining Fabrics: Theoretical and Practical Considerations", ICOM Committee for Conservation, 6th Triennial Meeting, Ottawa (1981), *Preprints*, 81.2.8.
2. G. Hedley, "Relative humidity and the stress/strain response of canvas painting: uniaxial measurements of naturally aged samples", *Studies in Conservation*, 33, no.3 (1988), 133-148.
3. G.A. Berger and W.H. Russell, "An evaluation of the preparation of canvas paintings using stress measurements", *Studies in Conservation*, 33, no.4 (1988), 187-204.
4. W. Conti and E. Tassinari, "Misura di "creep" su tele da rifodero", in *Problemi di Conservazione*, ed. G. Urbani (Bologna, Editrice Compositori, 1973), 168-182.
5. G.A. Berger and W.H. Russell, "Investigations into the reactions of plastic materials to environmental changes. Part I: The mechanics of decay of paint films", *Studies in Conservation*, 31, no.2 (1986), 49-64.
6. G.A. Berger, "Heat-seal lining of a torn painting with Beva 371", *Studies in Conservation*, 20, no.3 (1975), 126-151.
7. G.A. Berger, "Unconventional treatments for unconventional paintings", *Studies in Conservation*, 21, no.3 (1976), 115-128.

ABSTRACT

The traditional method of stretching used up to now has showed not to be suitable to adequately preserve canvas paintings, because of non-homogeneous forces distribution in the textile surface, and discontinuity of tension values imposed to the canvas in the course of time. A few methodological solutions have been worked out in order to reduce these two main damaging factors. One is a "buffer-surface" between the canvas painting and the stretcher which permits the absorption of the concentration of stress-strain generated by the expansion of the stretcher. If this device is regularly adopted in the maintenance of all canvas paintings, these could be advantageously protected from various damages. Another solution is a self-adjusting continuous tension mechanism planned in order to achieve a better distribution of forces and keep the canvas level. The effectiveness of these devices is supported by laboratory tests carried out on three specimen stretchers. Our procedures have resulted in a good conservation of the works of art even with lodging problems and in adverse microclimatic conditions.

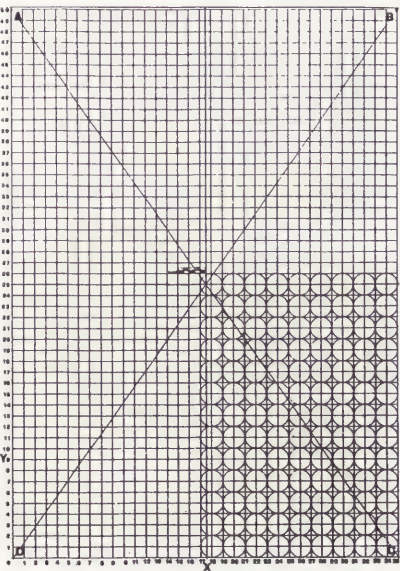


Fig. 1 - Grid drawn on the three specimen canvases

PRESERVATION OF CANVAS PAINTINGS
STRUCTURAL SOLUTIONS IN RELATION TO ENVIRONMENTAL CHANGES

Franco Del Zotto
RCA
Via Nanino 52
33010 Reana del Rojale (UD)
Italy

Introduction

Since about 1960 many researchers have taken a great interest in the conservation of canvas paintings and have tried to analyse the problems concerning the "paint layers-canvas-stretcher" whole (paint layers are size, ground and paint film). It is well known that each one of these materials has its own well defined chemico-physical identity, which gives equally different chemico-physical answers. Each material has its own elastic modulus and resistance to traction, compression and torsion, and shows its own tightening and dilatation curves in relation to R.H. and temperature variations. In order to preserve this composite structure properly, an equilibrium must be reached among the components (paint film-ground-structural support); the coexistence of different entities in the same system, i.e. the painting, makes this hard to achieve. The first macroscopic damage is the paint fissure or "craquelure", a cracking of the paint layers due to mechanical stresses. Such stresses can be considered the secondary product of other damage factors, still of environmental origin, working separately or, more frequently, together, namely chemical, physical or biological stresses. Our aim is to develop the analysis of the chemico-physical damages occurring to the work of art, and to suggest practical solutions suitable to the operative reality of conservation. The paint layer in a canvas painting is always strictly connected to other layers, namely ground, size and canvas. In order to evaluate occurring damages and to understand the mechanical phenomena that cause them, we must carefully consider the influence of canvas on paint film, and especially stretcher behaviour which, affecting the canvas, also works on the above layers. On the essential relationship between canvas and stretcher we shall present some practical solutions, worked out and tested by the Author, the utilisation of which can help towards the prevention and conservation of canvas paintings. To make the reading and understanding easier, we shall divide our analysis into two fundamental phases, each corresponding to a methodological solution. We shall first consider the problem of the non homogeneous distribution of forces on a canvas painting surface; then the discontinuity of values in the tension given to the canvas.

1 Stress-strain forces concentration and "buffer-surface"

As already mentioned, damages to canvas paintings largely arise from variations of microclimatic conditions, which, hardly ever suitable for the requirements of the art work, put in action the anisotropy peculiar to the composite structure, causing the manifestation of stress mechanical forces.

As far as the paint film is concerned, we can speak of two kinds of cracking: primary or drying cracks, due to inner stresses generated by the drying and evaporating process of solvents, and ageing cracks, that is mechanical cracks that develop late in the life of a paint film and that are almost completely ascribable either to mechanical stresses originating from inside of the structural system of a canvas painting, or to stresses arising from external pressures. Between stresses of internal source and those caused by external agents (i.e. the hand of man or any other object) there are others, not less important, imposed by the stretcher. Any canvas painting, relined or not, at first in good conditions of tension on a traditional stretcher is sooner or later destined to loose its original tension and consequently

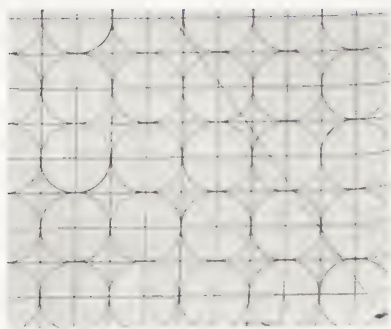


Fig. 2 - Stretcher 1: bottom corner grid after the elongation stress

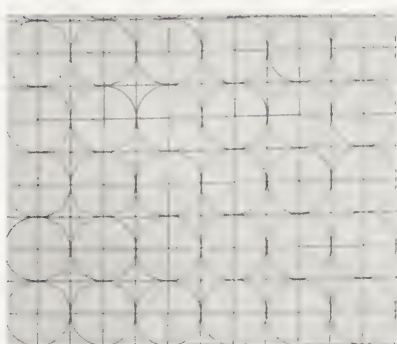


Fig. 3 - Stretcher 2: bottom corner grid after the elongation stress

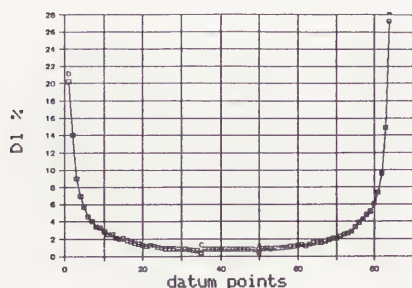


Fig. 4 - Stretcher 1: D-B direction 45° graph

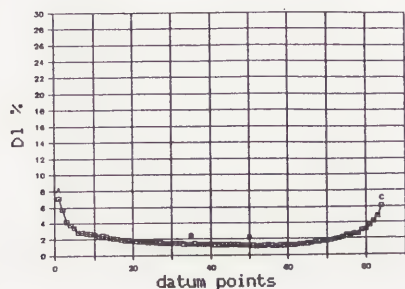


Fig. 5 - Stretcher 2: A-C direction 45° graph

its planarity. When the painting is regularly maintained, a tension regulating system by keys or metal turnbuckles is used to obviate this kind of damage. Each regulation, occurring whenever the canvas becomes slack, causes a constant enlargement at the corners, as the textile surface, nailed along the perimeter, can move freely only in that little corner place. Consequently, inside the canvas, because of the Poisson effect, not only traction forces (F_t) orthogonal to diagonals are generated, but also compression forces (F_c) along diagonals and perimeter. When, as time goes by, the plastic elasticity of the paint layers diminishes, the co-existence of such forces on the fabric causes in the paint layers cracks similar in aspect to ageing cracks. F_t and F_c can also cause damages to the fabric ranging from weakening to fiber breaking, and this occurs when the corner expansion exceeds the fibers cohesion strength.

1.1 The "buffer-surface"

In order to remove, or at least reduce, damage factors dependent on the traditional canvas-stretcher system, the first obvious thing to do would be to eliminate the fixed perimetrical nailing (nails, clips, sometimes glue too) to let the textile surface evenly expand, that is slide along the stretcher bars, whenever it needs to be stretched. With functionality, simplicity of realization, low cost and good aesthetic requirements in mind, a "buffer-surface" between the painting surface and the stretcher can absorb the non homogeneous distribution of forces generated by the stretcher expansion. It is a piece of lining (See fig. 17) or strip lining which is turned around the edges of the stretcher for an adequate length and then nailed on the back, thus avoiding the conventional nailing along the external perimeter of the stretcher itself. To prove the effectiveness of this theory a first series of comparative tests was carried out with the aim of comparing and analysing the stress-strain distribution in two standard samples: a conventional nailed canvas (Stretcher 1) and a "buffer-surface" canvas (Stretcher 2). The technique used in the experimental procedure was that of the grid (See fig. 1), formerly used by Hedley: a grid was drawn on the sized material, a stress was then applied to it and the consequent dimensional variations were determined and measured. With this procedure we can analyse the distribution of forces, not by single points but by larger surfaces.

1.2 Experimental test

For the experimental procedure two conventional stretchers (mortise and pin) were purposely made - 100 cm long, 70 cm wide, 3 cm thick - with corner turnbuckles. On the unstrained material, of strict weft, a thin layer of ground was applied to obtain an elastic and quite homogeneous membrane. The sized material was stressed on the stretchers in two different ways: on Stretcher 1 it was conventionally nailed by thick clips along the external perimeter; on Stretcher 2 it was turned around the edges and then nailed on the back leaving 12 cm of "buffer-surface". The edges of Stretcher 2 were purposely rounded and treated with an acrylic film in order to decrease the friction likely to develop between the material and the stretcher. The grid was drawn dividing the surface into squares 2 cm wide; in the bottom left corner a series of 4 cm diameter circumferences was also drawn, useful to a correct visualization of stress-strain elongation (See figs. 2,3). At this point the two samples were simultaneously, equally and slowly tensioned to obtain an average canvas elongation of 1.5%, and then their dimensional variations ($DI\%$) were measured. The preferential pattern lines extended on the whole textile surface, though with higher concentration along the perimeter of the stretcher.

Examining the 45° direction couple of graphs in Stretcher 1, and particularly D-B direction graph (See fig. 4) it was found that there is a more evident elongation ($DI\%$) on the corners, with a value of 20-28%, while in the middle there is a fall; in A-C direction there is a negative value of 1-2%, that shows the presence of F_c . Examining the 45° A-C and D-B direction couple of graphs of Stretcher 2 (See fig. 5), it was found that elongation at corners

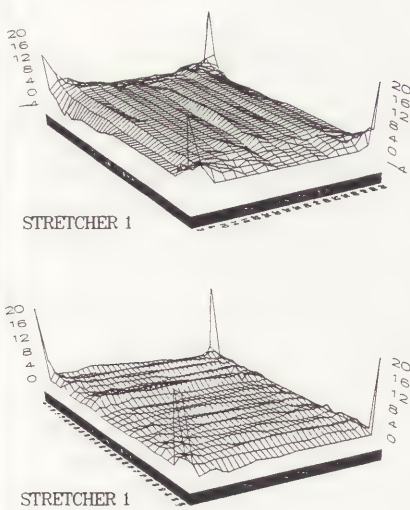


Fig. 6 - Stretcher 1: tridimensional X and Y axes graphs showing the per-cent elongation stress after stretching

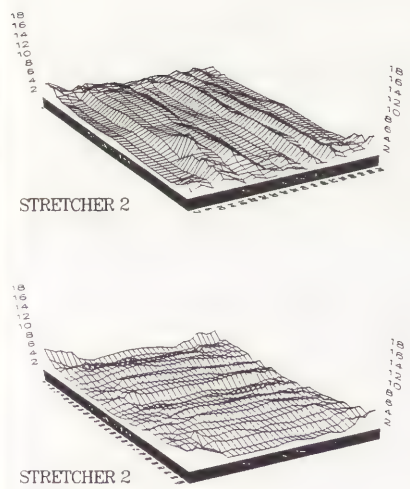


Fig. 7 - Stretcher 2: tridimensional X and Y axes graphs showing the per-cent elongation stress after stretching

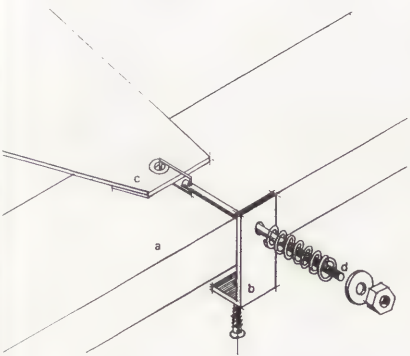


Fig. 8 - Self-adjusting mechanism for irregularly shaped paintings (e.g. oval) with fixed perimetrical size (e.g. frames, altars). a: stretcher, b: rust-proof metal blade, c: strip lining, d: self-adjusting rust-proof mechanism

went from a minimum of about 4% to a maximum of 7%. Furthermore no fiber yielding to F_c is shown.

To obtain a definite and complete view of stress-strain in the two stretchers, measurements were carried out also on X and Y axes, considering not the complete elongation of the sample line, but only the partial elongation variation (DI%) of the single segments of the grid (2 cm on the unstrained stretcher). For an immediate comparison and an easier evaluation of results, the graphs were elaborated into an X axis and Y axis tridimensional system for each stretcher. Examining the results of Stretcher 1 tridimensional graphs (See fig. 6) a big concentration of positive strains at corners is evident, with values sometimes higher than 30% on the first datum points, whereas elongation does not occur along the perimeter. Moreover it was found that the greatest elongation takes place along the grid diagonals. Moving away from the perimeter, the high peak recorded at corners diminishes quickly and places itself along diagonals towards the middle of the graph, where, however, elongation value is zero or near zero at many datum points. So F_t along the sides is short-lived and sometimes takes on negative value transforming itself into F_t . What was said before is particularly evident in the X axis tridimensional graph, where this peculiar distribution is justified by the Poisson effect which does not originate from a greater stress-strain on the Y axis, which has from calculations a smaller value than on the X axis, but from the concentration of major stresses at the corners. Very different are the results of the analysis of the tridimensional graphs in Stretcher 2 (See fig. 7). Clearly visible is the almost complete absence of positive high yielding value of the previous case: dimensional variation comes to a maximum of 5%. Furthermore along the whole perimeter there is a flow of transverse elongation, and moreover, there is no place on the specimen surface where the canvas is subjected to negative yielding. Comparing 45° graphs and tridimensional graphs of the two specimen, Stretcher 2 showed an improvement in the stress-strain distribution, more uniform and constant. Thus a simple technical trick (buffer-surface and nailing on the back of the stretcher), which sometimes allows the reutilization of the original stretcher, philologically and historically important as the front, can favour a homogeneous distribution of the forces generated by stretcher expansion.

2 Canvas non homogeneous tension and self-adjusting stretcher

The difficulty of maintaining canvas in conditions of even and plane tension is due to the anisotropy inherent in the composite structure "canvas-ground-paint film", that conventional stretchers cannot absorb in relation to microclimatic variations. Minimal microclimatic variations can cause heavy dimensional stresses in the structure, the more so if variations are frequent and sudden. In a day a work of art is usually exposed to more or less great variations; it is easily imagined expect how the concurrence of the arising stresses plus their repetition in time causes weakening, elongation, buckling, tear in the canvas and cracking, cupping, falling off in the paint film. A uniformly controlled environment could solve this problem by maintaining an equilibrium in the system. But if this solution can be applied in some cases (i.e. museums), it cannot find proper application on a vaste scale, hence the need of operating on the support structure. It has been ascertained that in order to reduce the above damages, the fabric material must be evenly, firmly and tightly stretched. When this stiffness yields, the paint layers affect the canvas underneath pushing it sideways. The canvas stiffness, defined as "E" (modulus of elasticity or endurance to displacement) increases with the stress exerted. The conservator's task is to supply the fabric with adequate, durable tension, sufficient to stop paint movements but not exceeding the maximum sustainable tension (MST, as Berger defines it). This aim cannot be achieved using conventional tension mechanisms (stretchers with keys or turnbuckles), because the canvas remains well tensioned, but as time goes by it is destined to become slack, and since these movements have a high frequency canvas deformation can be hardly accompanied by an equally frequent maintenance. The solution the Author suggests, based on a criterion also followed by other researchers, is to adopt a self-adjusting stretcher with a spring expansion mechanism.

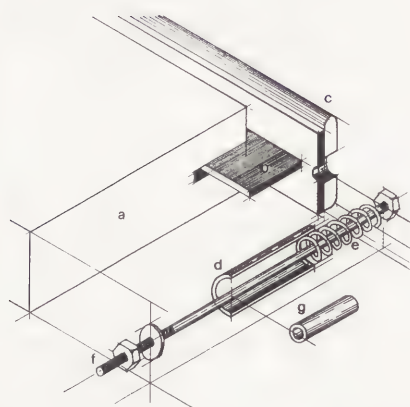


Fig. 9 - Self-adjusting mechanism for small paintings, because of T bar low resistance to torsion and flexion. Suitable for round shapes. Utilizable coupling with other systems. a: stretcher, b: T aluminium bar, c: wooden profile, d-e-f: expansion mechanism, g: screw guide-roll

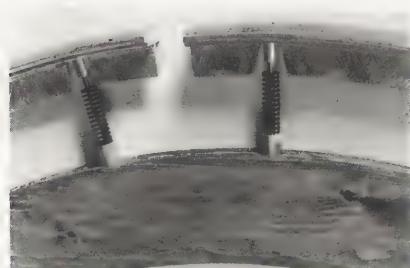


Fig. 10 - Detail of the T system in the round part of a painting



Fig. 11 - Detail of H bar system

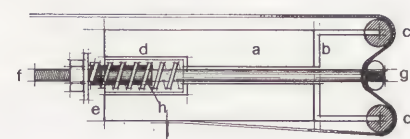


Fig. 12 - Self-adjusting mechanism, variant of H bar system. Suitable for paintings with fixed perimetrical size: cross-section

2.1 Self-adjusting continuous tension stretcher (*)

On the basis of the above data, referring to studies and research published so far, our laboratory has worked out a solution of its own. The tension mechanism project is based on criteria not only of functionality but also of simple realization, low costs and good aesthetics. The aim was to create an easy-to-make device, which would allow to conserve the traditional aspect of the back of a painting (See fig. 18). Some of the solutions worked out, after proper testing, have been applied on canvas paintings from XVI to XIX century (See figs. 8,9,10). In the course of our experiences we realized how difficult it was, and still is, to create a unique ideal stretcher. There is however a structure which corresponds more than others to the above mentioned characteristics. It consists (See figs. 11,12,13) of a rigid frame with movable edges, a low-friction sliding profile and a spring expansion mechanism. The frame is made of wood, with rigid corners so that it can be easily built, and with fixed joints which are therefore not yieldings points of the structure (besides wood the stretcher can be made in light materials, e.g. aluminium). The wooden frame supports H cross-section aluminium bars which slide along the perimeter in all directions. A mobile profile, made in strong wood (possibly made in other materials, e.g. plastic or PVC) with its surface treated to generate minimum friction with the fabric material, is fitted on the external face of the aluminium bars.

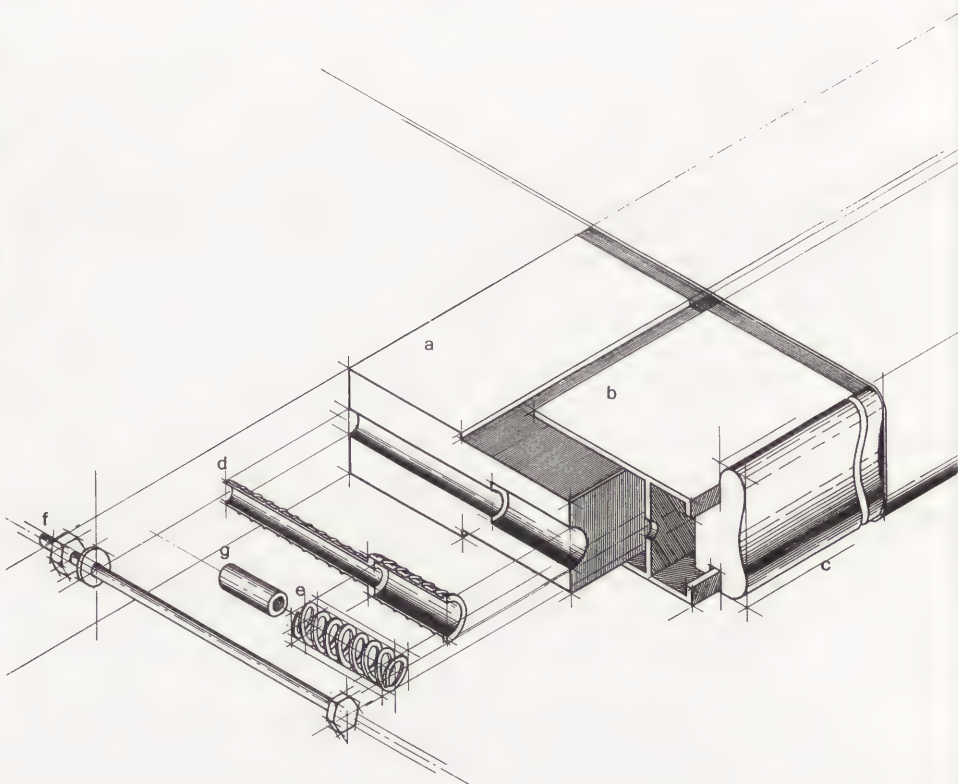
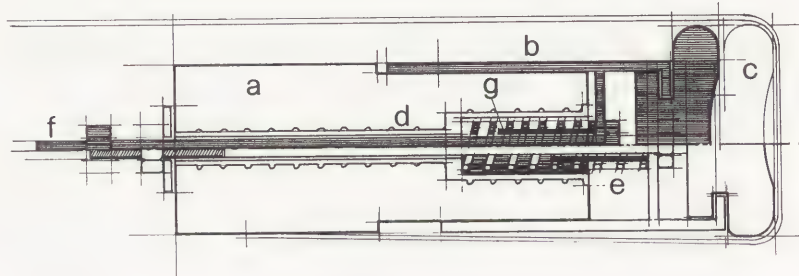


Fig. 13 - Self-adjusting mechanism with the best features, compatible with T bar system. Great facility of application. a: stretcher, b: H aluminium bar, c: low-friction profile, d: knurled sleeve, e: screw, f: bolt, nut and washer, g: screw guide-roll

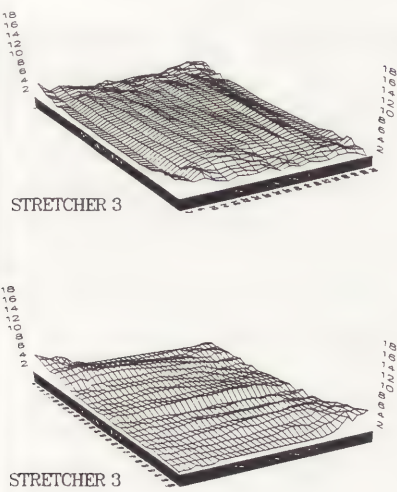


Fig. 14 - Stretcher 3: tridimensional X and Y axes graphs showing the per-cent elongation stress after stretching

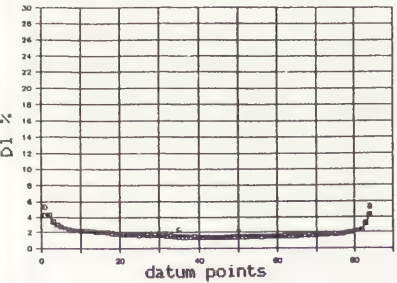


Fig. 15 - Stretcher 3: D-B direction 45° graph

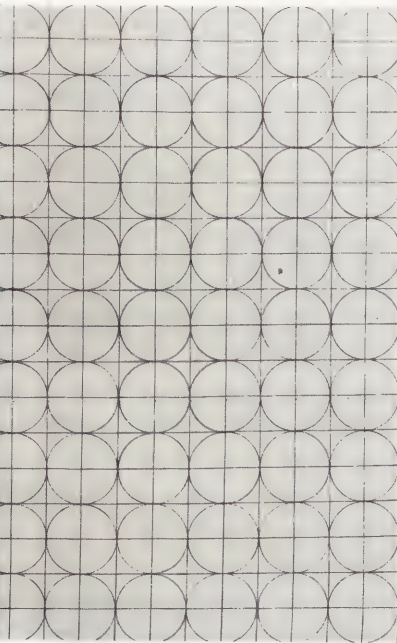


Fig. 16 - Stretcher 3: bottom corner grid after the elongation stress

In addition to keeping the canvas slightly detached from the stretcher, the wooden profile, because of its inner capability to run along the perimeter, helps the fabric slide on or with the elements themselves along all the stretcher edges, so as to create a better distribution of tension forces. The right continuous tension is provided by a controlled expansion mechanism thoroughly contained inside the cross-section of the wooden frame. Such a system consists of a rust-proof sleeve (aluminium, plastic or PVC) with a knurled external surface for close adherence to the wooden frame, so as to obtain a strong structure. Inside the sleeve, a threaded metal rod passes through the aluminium bar, enters a spring, guided by a roll, situated between the aluminium bar and the stretcher, and finally emerges on the opposite side of the frame (inner perimetrical side). A nut locked on the metal rod allows for millimetrical stroke adjustment of the spring, which is the element that regulates stretcher expansion by pushing the aluminium bar. The continuous tension mechanism is set along the frame according to the requirements of each painting. Thus the tension mechanism we suggest corresponds to the intended characteristics: the whole mechanism is located inside the frame, and the perimetrical aluminium slide is hidden by the fabric turned on the back. Because of the particular H-section, the aluminium bar can oppose strong resistance to flexion moment and torsion exerted by fabric tension, and the conservator can therefore build a stretcher with very reduced cross-section.

In a rigid conventional stretcher, when the inner tension of fabric exceeds the MST value because of R.H. and temperature changes, the canvas is overstretched and undergoes forced elongation to bring its tension back on the MST value. Our stretcher works especially on this kind of stress. It enables the canvas not to weaken because the springs in the mechanism can contract to reduce stretcher dimensions and so maintain MST continuous and E at a sufficient value. When, on the contrary, in a rigid conventional stretcher, the tension drops below its lower elastic limit, the canvas is no longer capable of resisting the expansion and contractions of the paint layers. The self-adjusting stretcher can prevent this tension drop with its dimensional expansion by perimetrical bars displacement: by restoring tension, an adequate value of E, necessary for a good conservation is likewise restored. Another fundamental point is that this mechanism is capable of adjusting maximum stretcher expansion with precision by means of work regulating screws. After the restoration of a painting and a period of adaptation to its environment, it is possible to regulate the screws to register the maximum MST value. The MST regulating screw system is useful as a security element in the case of impacts and tears: in this way tears will not increase because the spring continuous tension is locked at a safe value.

2.2 Experimental test

Another series of experimental procedures was carried out for a scientific evidence of the right tension exerted by our stretcher. As described in 1.2 chapter, a new structure - Stretcher 3 - was made using the above construction methodology; the low-friction profile was divided in parts 35 cm long. The enclosed graphs (See fig. 14) show the results of the measurements. For a more accurate evaluation of stretcher answers to different mechanical strains, some stresses were deliberately exaggerated: the imposed percent elongation stress was slightly higher than in the other stretchers, moreover two opposite corners were submitted to greater expansion. This fact caused an increase of expansion, graphically reproduced with peak ranging on the same row. Here stress-strain peaks are reduced in value as the ones in Stretcher 2 (See fig. 7), and this could be improved by cutting the low-friction mobile profile into shorter elements (about 10 cm long). Comparing Stretcher 3 and Stretcher 2 45° direction couple of graphs (See figs. 5,15) it is evident that in addition to a considerable reduction of corner maximum tension values there is a positive increase of the lowest values in the middle of the canvas. Compared with conventional stretchers, the self-adjusting continuous stretcher here illustrated offers a positive solution towards a good conservation of the composite structure (See fig. 16): it can contract or expand as necessary, without causing any variation of the inner tension, and consequently of E.

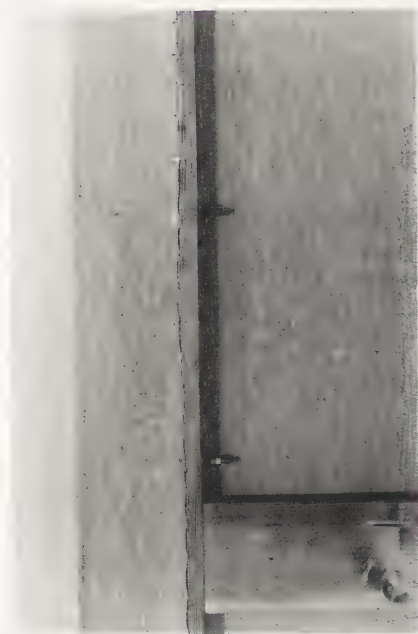


Fig. 17 - Detail of the buffer-surface on the back of a painting restored with the self-adjusting stretcher



Fig. 18 - Back of a painting restored with the self-adjusting stretcher

Conclusion

The damage factors in a canvas painting originate from the innate characteristics of the composite structure, namely the different responses of each layer to environmental variations of R.H. and temperature. This problem can be worsed by active or passive stretcher influence. For a good solution it is appropriate to operate not only on the microclimatic conditions in which the work of art lives (which can be difficult to achieve) but also and above all on the bond between fabric and frame, and on the stretcher realization technique. The fixed perimetrical bond, namely conventional nailing (active influence) must be avoided; it is essential to leave the stretcher free to modify its dimensions so that it can transmit a continuous tension to the fabric fibers (passive influence).

A simple technical device solves the first problem, that is turning the fabric around to the back of the stretcher with a buffer-surface (See fig. 17). This is easy to apply and can considerably reduce the increase in the concentration of forces. If the painting is quite small and the strip lining of sufficient elasticity, the buffer-surface device itself can positively act to maintain the requested continuous tension and above all can prevent the original painting from exceeding the maximum sustainable tension (MST).

The combination of this device with our self-adjusting continuous tension mechanism (See fig. 18) can prevent damages resulting from canvas tension variations. Such mechanism works well in favour of a homogeneous qualitative and quantitative forces distribution. We have found that the paintings we restored with the help of our devices and subsequently lodged in places with uncontrolled microclimate are up to now in very good conditions. Because of its security screws, the self-adjusting continuous tension stretcher can found its best application on those works of art lodged in unmoveable structures (wooden or marble altars high hanging frames), for which a routine maintenance can be neither continuous nor regular.

(* patent pending)

Acknowledgments

The Author thanks eng. A.Bruschi and Ms. F.Tonini for their co-operation.

References

1. S. Keck, "Mechanical alteration of the paint film", *Studies in Conservation* 14, (1969): 9-30
2. G. Hedley, "Some empirical determinations of the strain distribution in stretched canvas", ICOM, Venice, 1975
3. G. Berger, "The role of tension in the preservation of canvas paintings: a study of panoramas", ICOM, Ottawa, 1981
4. V.R. Mehra, "Minimizing strain and stress in lining canvas paintings", ICOM, Ottawa, 1981
5. J. Colville, W. Kilpatrick and M. Mecklenburg, "A finite element analysis of multi-layered orthotropic membranes with application to oil paintings on fabric", *IIC Preprints*, 1982: 146-150
6. M. Mecklenburg, "Some aspects of the mechanical behaviour of fabric supported paintings", *Smithsonian Institution*, 1982
7. G. Berger, "A structural solution for the preservation of canvas paintings", *Studies in Conservation* 29, (1984): 139-142
8. A. Diakowska-Czarnota, *Ochrona Zabytkow*, no. 37, 1984
9. G. Berger and W.H. Russell, "An evaluation of the preparation of canvas paintings using stress measurements", *Studies in Conservation* 33, no.4 (1988): 187-204
10. G. Hedley, "Relative humidity and the stress-strain response of canvas paintings: uniaxial measurements of naturally aged samples", *Studies in Conservation* 33, no.3 (1988): 133-148

ABSTRACT

A new method for treating the typically fragile and brittle water damage flaking of canvas paintings, locally, and without removal from the stretcher is outlined. There follows a discussion of the theoretical aspects of the interaction of moisture, during treatment, with each layer of the painting structure. The treatment strategy is derived from these considerations. The method works primarily by creating a moisture content gradient which is higher in the paint layer and lower in the underlying canvas. The technique has broader implications for moisture based treatments.

KEYWORDS

Canvas, Conservation, Flaking, Moisture, Paintings, Shrinkage, Softening

A NEW METHOD FOR TREATING WATER DAMAGE FLAKING

Gerry Hedley*, Caroline Villers, Robert Bruce-Gardner and Rhona Macbeth
Courtauld Institute of Art,
Somerset House,
Strand,
London WC2R 0RN,
U.K.

* Author to whom correspondence should be addressed

Introduction

It is a well known phenomenon that some paintings on canvas are prone to exhibit dramatic flaking of paint and ground when the canvas comes into contact with water. This behaviour is so notorious, so destructive, that paintings felt to be likely to respond in this way are known as 'shrinkers' or 'nervous', and include a large body of nineteenth century paintings.

Moisture Damage

We can now be fairly precise about why this kind of damage occurs. There are three distinct stages. First, water comes into contact with the canvas; almost immediately the fibres will swell and shrinking forces will be generated. Second, the moisture will penetrate through the canvas and begin to soften the size layer. And, third, when the size softens, the ground and paint buckle away from the canvas under the compressive shrinking forces. Being still in a brittle state they form fragile ridges of tented paint. Typically, there will be a time delay of 5-10 minutes between the first contact of the canvas with water and the appearance of the first flake.

Nineteenth century canvas paintings on commercially prepared supports are very vulnerable. This is because:

(i) The tighter the weaving the greater the canvas shrinkage force for a given yarn size. From about the second quarter of the nineteenth century the advent of power weaving for linen produced very tightly woven fabrics.

(ii) The size layer applied over these high shrinking fabrics often rests largely on the surface of the fabric rather than impregnating it. Because of this it forms a perfect release layer between the paint and ground, and it is also unable to restrict the canvas shrinkage in the same way as a size which impregnates the canvas

(iii) The typical commercial ground of the nineteenth century is a rather hard combination of lead white, chalk and oil which softens only slowly with moisture. However, the very hygroscopic size, which is a rather thin film, will soften far more rapidly. Consequently, when the size has become soft the ground will still be in a hard brittle state. No longer held in the picture plane, it will at once fail, by buckling away from the compressive forces generated by the canvas.

In combination these three factors mean that the classic nineteenth century canvas is virtually designed to generate delamination of the ground soon after contact of moisture and canvas. Some things can help resist this damage, such as very tight stretching of the painting, or thick paint layers which could oppose buckling. Additionally, the shrinkage forces are related to the amount of water taken up by the canvas. Evidently when liquid water falls onto the back of a painting, the canvas is likely to be saturated and disaster will soon follow. This is another argument for the use of protective backboards which can keep the canvas dry. But, in certain treatments, where the conservator uses moisture, it means that it is very important to control the volume of moisture presented to the canvas, so as to restrict shrinkage forces.

Unfortunately, accidents involving moisture still seem to be rather common, and the resultant flaking damage represents a challenge to the conservator. It is the kind of damage for which there is no established treatment. Some favour lining with glue/paste adhesive, some, heroically, opt for the 'burnt finger' treatment, and others, on occasion, transfer the painting. The treatment we have developed is a new option. It has enabled us, with a minimum of equipment, to treat a number of water damaged paintings without lining or even removal from the stretcher.

Moisture Softening

We arrived at our treatment by reconsidering the problem from first principles (1). What confronts us in this kind of flaking damage are hard, fragile, brittle flakes of paint and ground which are raised away from the canvas. Re-adhering the flakes would be much simpler if the paint could be made soft and compressible. We know moisture and low heat tends to soften dried oil paint films. This is, after all, the fundamental basis of the glue/paste lining technique. So, if it were possible to raise the moisture content of the paint and ground, it ought to soften and become more amenable to flattening. In fact, all three components of paintings, the canvas, the size and the paint are softened by uptake of moisture. But the effects are differentiated; the canvas and size, being extremely hygroscopic, are very strongly affected by moisture, whereas, though oil paint films ultimately soften, they need to come into equilibrium with much higher relative humidities to do so.

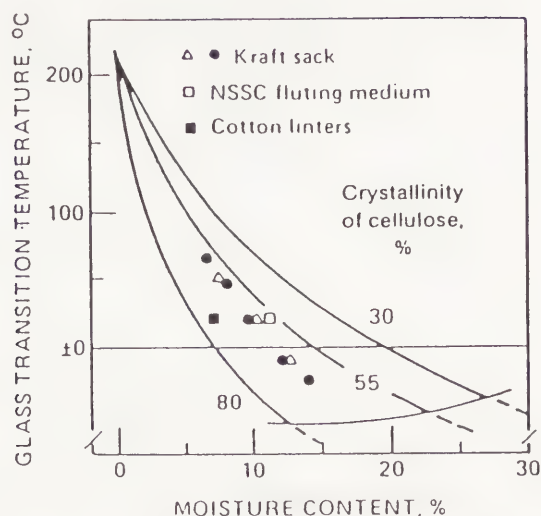


Figure 1 The change in glass transition temperature with moisture content for cellulose of different degrees of crystallinity. Data reproduced from Salmen and Back (2).

TMA Normalization: mek17
Sample Height: 0.020 mm
Fri Oct 27 17:25:22 1989
RSG over CaCl₂/Si oil 2a
(Normalized)

PERKIN-ELMER
7 Series Thermal Analysis System

TMA Normalization: mek16
Sample Height: 0.012 mm
Fri Oct 27 16:53:40 1989
RSG over H₂O/2(a,b) H₂O/Si oil
(Normalized)

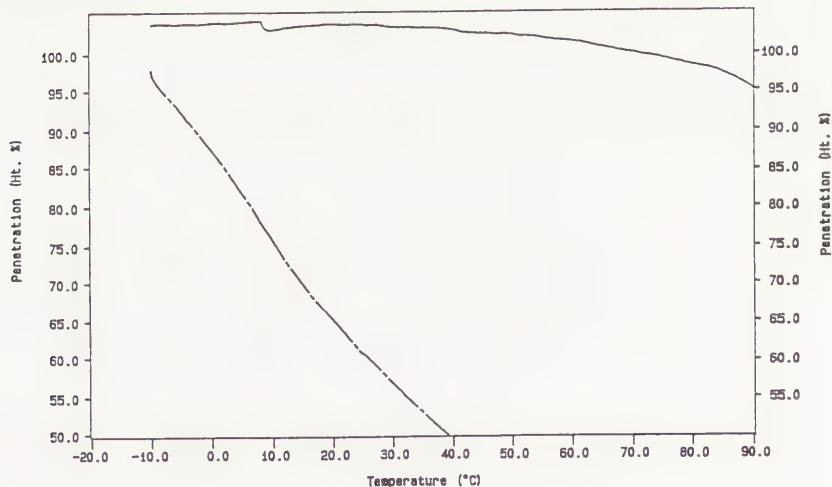


Figure 2 The compressibility of a film of rabbit skin glue when dessicated over CaCl₂ and humidified over water.

TMA Normalization: 1866g
Sample Height: 0.199 mm
Fri Nov 18 11:43:23 1988
Ground 1868 oil/gelatin (dry)
(Normalized)

PERKIN-ELMER
7 Series Thermal Analysis System

TMA Normalization: 1866w
Sample Height: 0.228 mm
Fri Nov 18 14:20:52 1988
Ground 1868 oil/gelatin wet
(Normalized)

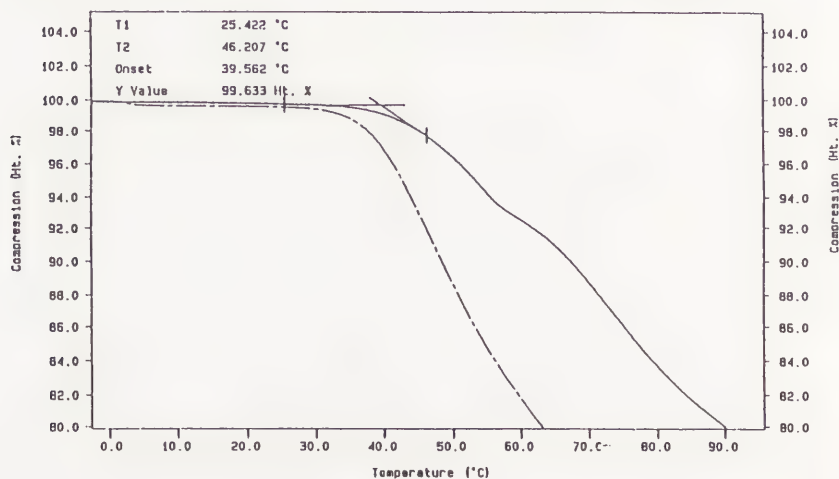


Figure 3 The compressibility of a nineteenth century commercial ground layer when conditioned to ambient conditions (approx 50% RH) and when wet with water.

In qualitative terms we can think of the canvas and size layers as being substantially softened by the time they are in equilibrium with 80-85% RH, whereas the paint films will need to come to equilibrium with RH values which are very likely above 90%. What is more, the sorption rate of the denser, more compact, oil layers will be much slower than that of the hydrophilic canvas and size. These differences are graphically presented in Figures 1-3.

It can be seen from the data of Salmen and Back (2), in Figure 1, that the glass transition of cellulose, which starts at the very high value of 230°C, falls and rapidly approaches room temperature as the moisture content rises. In Figure 2, the well known behaviour of dry and moist rabbit skin glue is contrasted, as a function of temperature. Figure 3, shows the response of a nineteenth century ground when at equilibrium with an RH around 50% and when soaked in water. The point to note is that the ground is softened, but that the effect is not as overwhelming as that which occurs in canvas and size. Put simply, this means that to get the paint soft, we shall have to raise its moisture content to an equilibrium with a high RH, and for maximum effect, we should also raise the temperature to around 40°C.

Humidification from above

At first sight this, theoretical definition seems to present us with problems rather than a solution. It seems to imply that we should use moisture, and quite a lot of it, on a painting which moisture has already damaged. Indeed, the common ways of raising the moisture content of paintings are not going to help us in this special case of a painting on a shrinking canvas. If a humidity chamber is used, the whole of the painting will be taken to equilibrium with the same RH; but, if we raise the RH high enough to soften the paint, we shall shrink the canvas first and perhaps cause further damage. Nor do humidity controlling multipurpose tables seem to help, since they present moisture first of all to the canvas support, and so, they too, are likely to set up shrinkage forces in the canvas. Glue/paste lining in the hands of a skilled practitioner might conceivably manipulate the variables for success, but few would feel confident. Given these difficulties in using moisture, restorers have often avoided it altogether and opted simply to use the softening effect of heat. Figure 3 shows that this may work, but that the temperature must be rather high - hence the burnt fingers!

In fact, what we really need is a moisture gradient in the painting which is high on the paint side and lower at the canvas. The simplest way of achieving this is to humidify from the front of the painting, and preferably to do so locally just in the areas of damage. Curiously, the very seriousness of the damage actually helps us. For the flakes of paint are normally tented and fractured; this means that both the paint surface and ground surface are available to absorb moisture, and this is to our advantage because it should be much easier to raise the moisture content in a tented flake than it would be in an area which was merely cupping. Equally important, if we can do the treatment locally, we only risk raising the moisture content of the canvas directly below the paint flakes, which has already shrunk and which therefore will not be so responsive to a second moistening. Another helpful factor is that the shrunken canvas is not going to be too hard to extend a little, both because it is no longer 'locked' by having ground attached to it, and because it is a property of a shrunken canvas that it is initially a little easier to extend than it was prior shrinking. All these considerations make it possible to treat the flaked areas by the remarkably simple expedient of humidifying them locally with damp blotting paper.

Before describing the treatment in detail it is worth noting that humidification from above does have a certain history. Quite obviously, the technique of aqueous facings in glue/paste lining is one which raises the moisture content of the paint (as well as applying forces to press down cupping when the paper contracts). There is a closer parallel to be found in the method by which sturgeons glue is used to lay flakes. It is simply brushed on through tissue paper and the flaking area is gently pressed down. The technique has acquired a kind of mystique, but it is not hard to see why it can work. Sturgeons glue, as used, is mostly water, but the glue reduces the surface tension of the water (3) and will help it to wet paint films more easily, it will therefore soften paint quite quickly. Though a weak adhesive, it is perfectly strong enough to re-adhere detaching flakes and will also exert some contracting forces as it dries. The limitation with sturgeons glue is, that for the harder and/or thicker flakes, it will not work quickly enough and the paint is liable to break up. The technique we favour has the advantage of allowing us to be quite sure the paint has softened before proceeding with flattening and re-adhesion.

Treatment procedure

This treatment exploits the differential response to moisture of the various component layers of a painting; it is localised to the area of damage and need not entail removing the painting from its stretcher. The general method is straightforward and no elaborate equipment is required: water, blotting paper, Melinex and a heat source will be sufficient.

Typically, pieces of blotting paper approximately 6 x 8 cms. in size are lightly moistened and placed directly over the tented ridges and immediately surrounding paint. They are covered with Melinex to create a miniature humidity chamber and left in position until paint and ground reach such a high moisture content that they soften enough to be pressed down easily with the finger. The size, which has acted as the release layer between paint and ground, will be swollen in the process. The length of exposure required to achieve this state may vary between five to sixty minutes and, in practice, depends on film thickness, pigment type and medium content (see Figure 4).

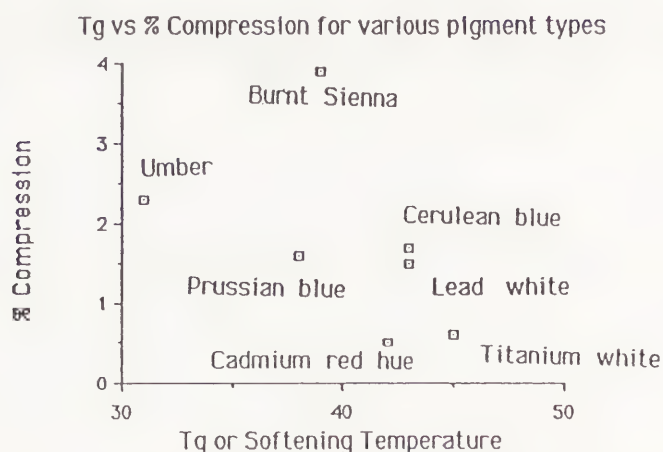


Figure 4 The widespread range of compressibility and softening temperatures likely to be encountered in different paints. Deformations in paints which lie in the top left will respond most readily, whereas those in the bottom right will be more resistant. Tested paints are eleven years old, naturally aged, oil paints.

An area of impasto or sky, with a high proportion of lead white pigment and low medium content, will take much longer to soften than a thinly painted passage of dark background consisting of mainly umber and earth pigments, which have a high medium content. It is likely that a normal nineteenth century commercial white oil ground will require an exposure time beyond twenty minutes. In some cases the tented ridges may be unbroken and this will also affect the length of treatment since the moisture will be delivered only to the upper paint surface, rather than paint and ground simultaneously.

This is also the case with cupped paint where, though the ground remains more attached to the support, the cupped paint has been successfully corrected using the same treatment strategy. In these situations, where the paint is not so vulnerable that it is likely to be crushed or dislodged, a rather neater method of delivering the moisture may be employed: a thick aqueous gel, for instance, sodium carboxy methyl cellulose, is spread onto the centre of a piece of felted polyester, approximately 15 x 15 cms., and this is placed onto the paint surface and, as before, covered with Melinex. The gel does not penetrate the fabric, so the paint film is free from direct contact with water, the exact nature of the gel will influence the maximum relative humidity attained under the Melinex cover.

Low heat will enhance the softening of the paint and ground at this elevated moisture content. We use either a hot spatula, or hot air through a film of Melinex, at temperatures around 30-40°C. An infra-red bar heater above the painting could also be used and, like the hot air, would have the advantage that the paint is softened before any pressure is applied. As with the application of moisture the surrounding paint must be warmed in the same operation as the tented ridges. Although only low heat is needed, at high moisture content there is still a danger of over-softening leading to deformation of the delicate paint surface and special care should be taken to guard against this. The restorer must judge the point at which the paint and ground have become sufficiently plastic for the tented or cupped paint to be pressed down without fracturing. If it remains brittle the period of humidification should be extended.

The use of moisture, particularly together with heat, does bring a risk of blanching either paint or varnish, or both, and, as normal, the restorer must test an appropriate area before proceeding. To reduce the risk to the paint a temporary varnish can be used.

Re-adhering the paint and ground

In order to re-adhere the tented or cupped paint we have generally chosen an aqueous adhesive, such as gelatine, either as a solution or gel, or sturgeons glue. A solution of sturgeons glue has the advantage of lower surface tension than gelatine and, consequently, better wetting of the surfaces to be joined. In either case this type of adhesive allows for easy manipulation of flakes. When using sturgeons glue we do not apply it in the usual way through acid free tissue paper as the paper frequently bonds too strongly to the paint surface for it to be removed easily and safely.

Only a small amount of aqueous adhesive is needed since the water content enhances the reactivation of the painting's original size layer. In some cases the period of humidification may achieve this alone, and in one example, an English portrait on a Roberson's prepared canvas dated 1844, just the reactivated original size, without additional adhesive, was used to adhere the flakes to the support. In fact, in most paintings that are prone to this type of tented cleavage, the size layer can be expected to contribute to the process of re-adhesion.

If the tented ridges are not fractured it may be impossible to get any adhesive to penetrate from the front. In such a case, a 1950's oil painting, sturgeons glue was introduced

from the back of the canvas. This has potential dangers as the reactive canvas is once again saturated with water and the advantage of a treatment designed to avoid over-humidifying the canvas seems to be lost. This treatment is entirely time dependant and it is critical that the canvas is dried out so rapidly that there is not enough time for shrinkage damage to occur. The method involves the use of the small low pressure Mitka-type table placed directly below the treated area, so that the high air flow dries the canvas within two to five minutes, and the pressure pulls the previously humidified flakes down, as well as restraining fabric shrinkage to some degree.

Once the tented flakes have been successfully treated it is important to consider how broad an area of delamination may have occurred, as, not surprisingly, this type of water damage can also cause extensive blind cleavage. In discussing the treatment it has been emphasised that, not only the area of tented ridges, but also the immediately surrounding paint should be exposed to humidity and heat; this is required because in pressing the softened flakes compressive forces may be developed in adjacent areas of paint, where the bond to the canvas is either severely weakened or non-existent. Theoretically, it could buckle or fracture if not previously softened (see Figure 5).

a)



b)

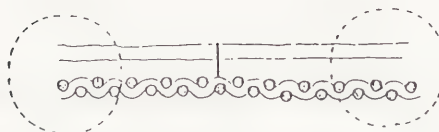


Figure 5 (a) Schematic representation of moisture damage flaking, and (b) corrected flakes with areas of potential blind cleavage marked by dotted circles.

In order to deal with the blind cleavage some sort of impregnation from the back of the canvas may be required. In situations where we do not want to use an aqueous adhesive we have chosen Plexisol B550 (n-butyl methacrylate) in white spirit, for its low viscosity, excellent penetration, and low heat seal temperature.

Conclusion

To date, seven severely water damaged nineteenth and twentieth century paintings with tented cleavage, and four with serious local cupping have been treated successfully following these general principles. The method is both minimal and highly controlled: the painting is not removed from its stretcher; only those areas that are likely to benefit are exposed to humidity; the treatment is localised to the regions of damage and can be varied according to paint type and thickness; the minimum amount of new adhesive is introduced. The significance of the treatment goes beyond the challenging problems it has been devised to deal with: the principle of humidification from above has important implications for the design of multi-purpose tables and the treatment of paint deformations in general. Current research is concentrating on exploring these possibilities.

Acknowledgements

We should like to acknowledge the assistance of Marianne Odlyha in obtaining the data in Figures 1, 3, 4, and to thank Perkin Elmer Ltd (Beaconsfield) and, in particular, Dr. T. Lever, for lending us the TMA 7 thermal mechanical analysis equipment.

References

1. G. Hedley, and M. Odlyha, "The Moisture Softening of Paint Films and its Implications for the Treatment of Fabric Supported Paintings," in *Conservation - Restauration des Biens Culturels Recherches et Techniques Actuelles*, A.R.A.A.F.U., Paris, November, 1989.
2. N. L. Salmen, and E. L. Back, "Moisture-dependent thermal softening of paper, evaluated by its elastic modulus," *Tappi*, Vol. 63, No. 6, p. 117, June 1980.
3. D.A. Dyer, and M.A. Haupt, "An Examination of Animal Glues," Queens University Research Project, 1988.

SUMMARY

The picture "Joseph and his Brothers", painted 1657, was lined twice in the 18th century. The glue was apparently an excellent substrate for moulds threatening the paint layers. The moulds were isolated and their enzymatic activities investigated in detail. The deleterious (lipolytic) activity of these moulds, associated with the presence of glue as substrate, was proven to cease when the glue was removed. Therefore, the conservation consisted of efficient removal of only the glue using a new enzymatic preparation originating from Antarctic krill. After a short exposure nearly all the glue was hydrolysed. The minor glue residues were finally dissolved using amylase alone in order to protect the original impregnation of the canvas.



Photo 1

The work of Gebrand van de Eeckhout "Joseph and his Brothers".

Canvas dimensions: 197 x 176 cm
Inscribed a tergo G.v.Eeckhout. fe au 1657

Skokloster Palace, No. 11459.

ENZYMATIC HYDROLYSIS OF THE LINING PASTE IN EECKHOUT PICTURE "JOSEPH AND HIS BROTHERS" BY KRILL ENZYMES.

Frantisek Makes
Royal Armoury
Skokloster Palace
Hallwyl Museum
Sweden

Introduction

In the 18th century the picture was lined with a mixture of flour, glue and lard. A second canvas lining added later, was overglued with paper; the lining paste consisted of flour and glue. Mould growth was mainly localized in the paint layers which contained hygroscopic pigments. These spots looked very similar to turbid varnish but, when magnified, there was no doubt about the presence of mould. The painting had a brown-yellow varnish and was covered with grime. A preliminary examination revealed the occurrence of free fatty acids. Due to the difficulty of ascertaining in the origin of these fatty acids, an investigation with lipolytic enzymes was performed in order to establish the hydrolysis pattern in the linings of the paint layers and the glue.

Painting technique

The entire composition was painted on a double ground: an orange-red layer (lower layer) and a greyish-brown layer (upper layer). A similar ground is found i.e. in the painting "The Great Self Portrait of Rembrandt" (1651), located in the Kunsthistorisches Museum in Vienna. This type of double ground is also described by van Wetering, Kühn and Sonnenburg (1-3). The painting consists of very thin paint layers. This can be observed for example on Joseph's head, where the layers shift from very thin, transparent layers of white lead to thick layers which completely cover the ground. In this manner a broad spectrum of tones was achieved, creating the depth and volume of the painting. X-ray photography shows this technique (Photo 2).



Photo 2

X-ray photograph
of the Joseph's head

Assay of surface active substances in the painting

A method of for detection of pyrogene with distilled water previously purified by active charcoal has proved efficient. Pyrogene consists of dead micro-organisms or products of microbial metabolism as a result from mould activity. It has been found that the presence of pyrogene can be detected polarographically in the same way as the presence of surface active substances. By pyrogene with water previously purified by active charcoal on a cadmium-ion wave the polarographic maximum is lowered.

The presence of surface active substances manifested itself by the shape of the polarograph curve. The pattern of purified water characteristically shows that the current at the potential - 0.82 V purified SCE * suddenly increases to a maximum and then slowly decreases towards a negative potential. On the contrary, the surface active substance shows the diffuse current of a normal wave. The tests were performed with 3 ml H₂O from the washed painting surface, together with 3 ml 2 M NH₄Cl and 0.1 ml 0.1 M CdCl₂.

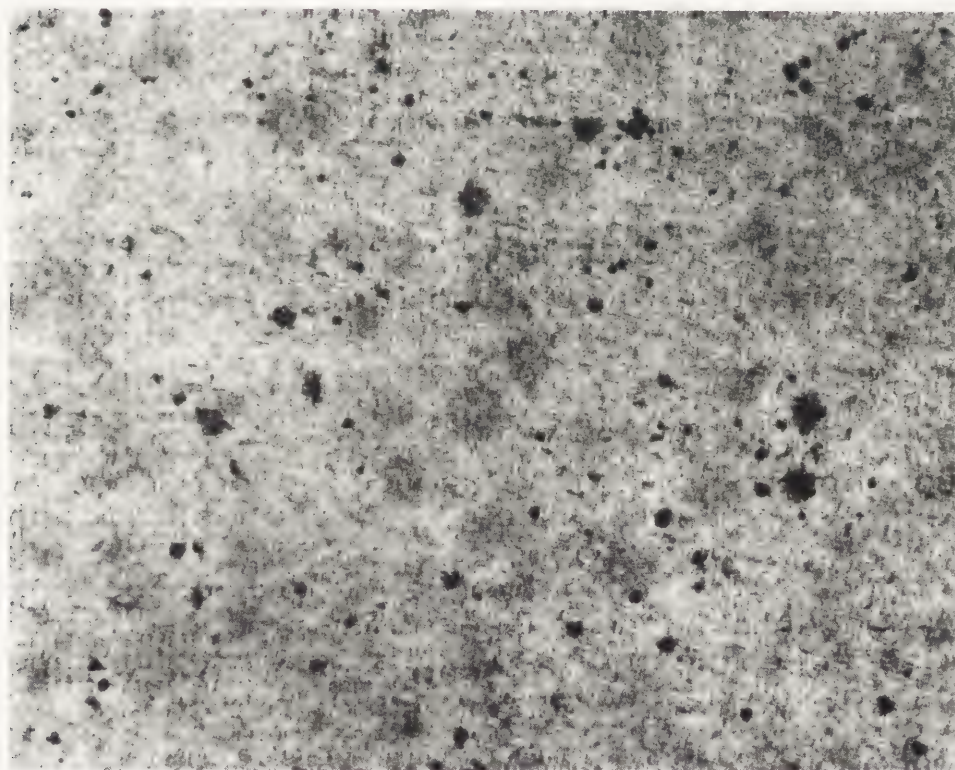


Photo 3

The second canvas lining (UV photo)

Growth conditions/enzymatic activity of moulds isolated from the painting

The moulds originating from the painting were inoculated on Sabaraud glucose agar. After five days the mycelia were separated from the substrate by filtration and the filtrate inoculated on three different substrates:

- 1 Rapoport's medium + artificial imitation of the paint layer on the painting
- 2 Rapoport's medium + artificial imitation of the lining paste on the painting
- 3 Rapoport's medium + lining paste from the painting.

The results are shown in Table 1. The mycelial mass was then removed by filtration/centrifugation and the relationship between the growth conditions and the enzymatic activity is shown in Fig 1.

The lipase activity varied with temperature and reached a maximum at 10°C.

* SCE - saturated calomel electrode

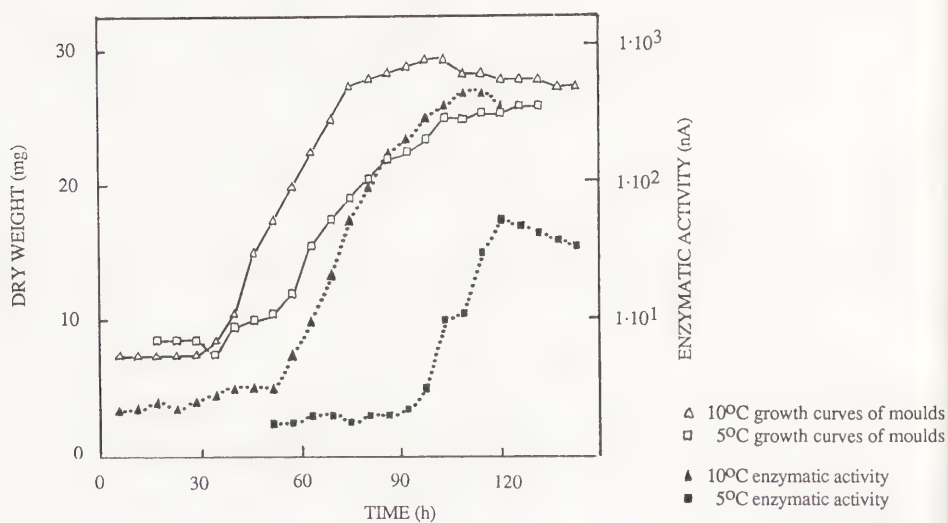
Table 1

Enzymatic activity of moulds from the painting expressed as function of the different substrates

Substrate	Enzyme activity
R + dry oil (paint layer)	3. 160E + 00 nA
R + artif. imit. lining paste	2. 796E + 02 nA
R + lining paste	6. 200E + 02 nA

Fig 1

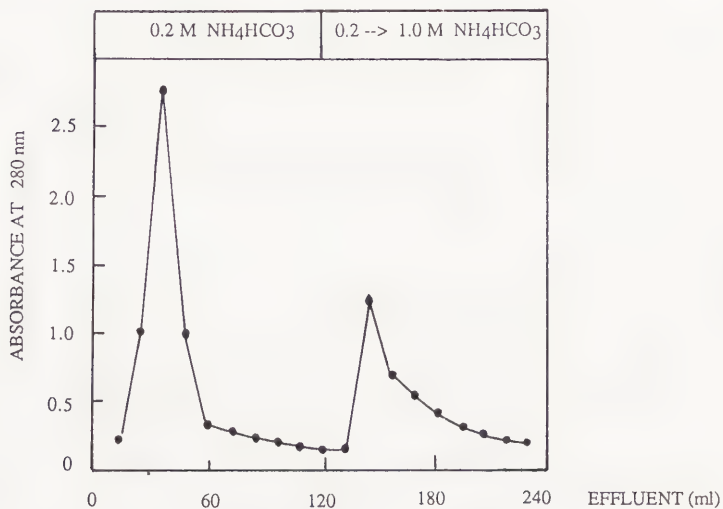
Growth curves of moulds from the painting at two different temperatures related to enzymatic activity.



The samples from above were run through a diethylaminoethyl (DEAE) cellulose (DE 52, Whatman Ltd) column, previously equilibrated with 0.2 M NH_4HCO_3 -buffer, pH 8.0. The samples was dissolved in the buffer, and applied to the column. After washing with 120 ml of the buffer, the adsorbed enzyme was eluted with a linear gradient of 0.2 to 1.0 M NH_4HCO_3 in all 120 ml (Fig 2).

Fig 2.

Ion-exchange chromatography of mould lipase from the painting on DEAE-cellulose, absorbance at 280 nm.



For further purification the active fractions were dissolved in 1 ml of 0.05 M NH_4HCO_3 buffer (pH 7.9) and purified on a Sephadex G-100 column (Pharmacia, Uppsala, Sweden).

Lipase assay

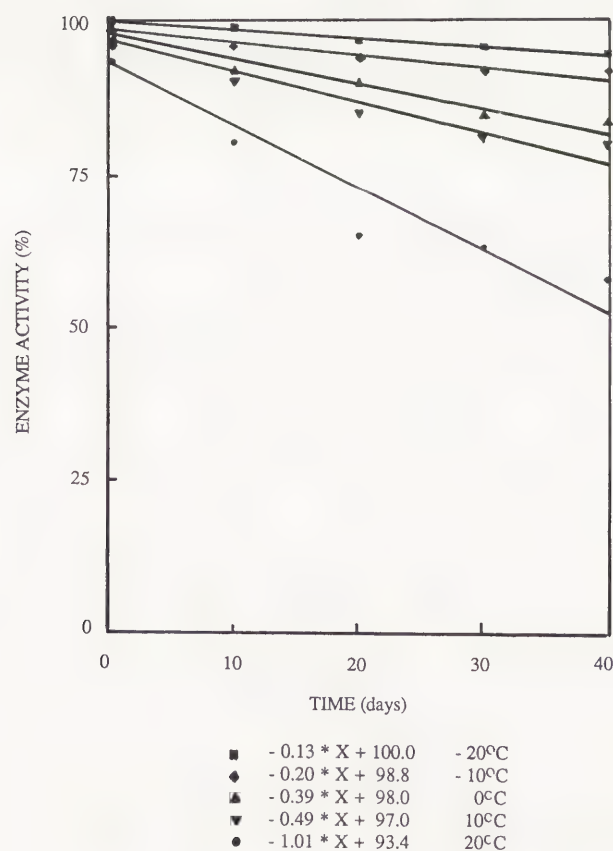
The 2-naphthol, liberated by enzymatic hydrolysis of the substrate (2-naphthylmyristate), reacted with a mixture of H_2SO_4 and NaNO_2 .

The resulting 1-nitroso-2-naphthol was reduced on a mercury drop electrode thus giving a wave proportional to the enzyme activity. The enzymatic activity was expressed as μmol of substrate/sec.

As Skokloster Palace is not heated, extreme fluctuations in relative humidity and temperature take place. Therefore, the lipase stability within a temperature range, based on mean measurements from Skokloster was determined. The enzymes were stored at -20°C , -10°C , 0°C , 10°C and 20°C for one month (Fig 3).

Fig 3

Stability of purified mould lipase from the painting after one month of storage at different temperatures expressed in terms of initial reaction velocity.



It could be demonstrated that the spring season (April-May) where relatively elevated temperatures are associated with high humidity constitute the optimal period for microbial growth and their enzymes. The lipolytic activity was exclusively localized in the glue that had come to the surface through the cracks (photo 4). Thus no harmful effect of mould enzymes on the paint layer could be observed when the glue was removed. Consequently, the efficient removal of glue was a goal of the restoring work.

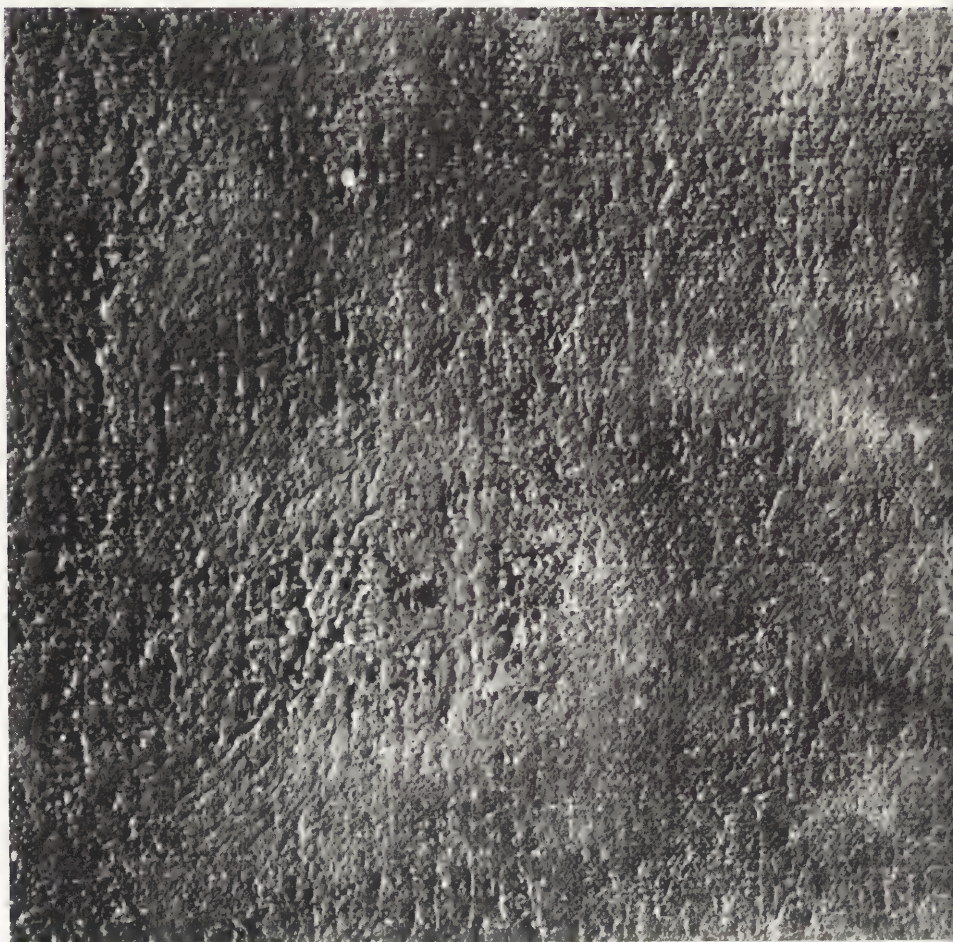


Photo 4

The mould on the
paint layer

Painting conservation

The most important task of the whole conservation treatment was the elimination of glue absorbed by the original canvas, and in this manner to eliminate the substrate for the microbial growth. An enzymatic removal of the glue was performed in two steps. In the first step, a enzymatic preparation of krill enzymes in CMC * was used.

Antartic krill, a shrimp-like crustacean, is a key organism of the Antarctic convergence. The unique ecological situation of krill, with a limited food supply during a substantial part of the year and an abundance in the short summer season, has resulted in the development of an unusually effective digestive system in this animal. The krill's multi-enzyme system contains proteolytic/carbohydrate-splitting and lipolytic enzymes (4). The krill enzymes were previously used successfully in the enzymatic consolidation of Archimboldos famous portrait of Rudolf II- "Vertumnus" (5).

To prevent the multi-enzyme krill preparation from reaching the original impregnation of the canvas, the glue residues were hydrolysed by amylase at the second and final step of the conservation treatment.

* CMC - carboxymethylcellulose

Conclusion

The picture "Joseph and his Brothers" was painted by a Rembrandts's disciple G.v. Eeckhout in 1657. The painting was lined twice, for the first time in the 18th century with flour, glue and fat, and later with paper together with flour and glue.

The painting is executed on canvas which was isolated from the paint layers by glue. The ground layer consists of a double-ground, which is typical for Dutch paintings of 17th century.

In the paint layers, three types of mould, *Penicillium*, *Trichoderma* and *Mucor*, were identified. The moulds were generally found in areas where hygroscopic pigments were present as a part of the paint layer.

In preparation for the restoration work, the enzymatic activity of the moulds, isolated from the paint layer, was studied in detail. The lipolytic enzymes from the moulds were purified and further characterized by chromatographic techniques.

As the Skokloster Palace is not heated, extensive variations in temperature and relative humidity take place during the year. It was therefore important to establish the lipase activities from the moulds within the temperature range found at Skokloster. The results point to the fact that the most critical time period for their hydrolytic activities in the painting is the short spring season (April - May) with relatively high humidity and temperature.

Consequently, the target of the conservation was an efficient removal of the glue, a substrate for the microorganisms and their deleterious metabolites. To achieve a mild breakdown of the glue, enzymatic hydrolysis with a new multienzyme preparation isolated from Antarctic krill was used. After a short exposure to the krill enzyme preparation nearly all glue was hydrolysed. In order to protect the original impregnation of the canvas, the minor glue residues were finally removed by amylase only.

Reference

- 1 van de Wetering E
Studies in the workshop practice of the early Rembrandt
PhD thesis, University of Amsterdam, Amsterdam 1986
- 2 Kühn H
Untersuchungen zu den Pigmenten und Malgründen Rembrandts,
durchgeführt an den Gemälden der Staatlichen Kunstsammlungen Dresden
Maltechnik-Restauro 4, 223, 1978
- 3 von Sonnenburg H
Rembrandts "Segen Jakobs"
Maltechnik-Restauro 4, 217, 1977
- 4 Osnes KK
Peptide hydrolases of Antarctic krill, *Euphausia superba*
PhD thesis, Trondheim, The Norwegian Institute of Technology 1985
- 5 Makes F
Enzymatic consolidation of the portrait of Rudolf II as "Vertumnus"
Göteborgs Studies in Conservation 1. Acta Universitatis Gothoburgensis,
1988

ABSTRACT

A possibility was found to conserve the canvas of paintings substantially reducing its hygroscopicity without changing the colour, texture, vapour penetrating and physico-mechanical characteristics.

As a result of this treatment the canvas hygroscopicity is reduced so much that, in the course of restoration, there is no penetration observed to the reverse side of the painting of restoration (sturgeon) glue aqueous solutions. This makes it possible to eliminate the stage of lining the painting on a new canvas and carry out restoration by using much lesser quantities of the restoration glue leaving the reverse side of the painting open, which is very often valuable as the available signatures, inscriptions and dates remain safe. Another very important aspect of the painting canvas conservation is its better preservation in the conditions of variable temperature and humidity occurring in museum expositions and storages.

KEYWORDS

Canvas, hygroscopicity, moisture barriers, restoration glue, organo-silicon.

TECHNIQUE OF RESTORING PAINTINGS ON CANVAS WITHOUT LINING

I.V.Nazarova, E.L.Malachevskaya, L.I.Yashkina
10 Krestyanskaya Pl., VNIIR
Moscow, 109172,
U.S.S.R.

Introduction

The required climatic conditions are not maintained in the majority of museums, both in showrooms and storages containing oil painting on canvas. There are significant changes in humidity due to seasonal fluctuations and large number of visitors. The painting canvas is the first to react to these changes by adsorbing moisture and in so doing increasing its size and sagging, and then returning to its original size. Permanent deformations of the canvas lead to a disruption of its adhesion to the ground and paint layer resulting in the ground and paint layer scaling off the canvas, in its rigid cracks and rigid craquelure.

Thus the paint layer of a painting is the first to suffer because of the canvas deformation. It follows that the most important task in preserving the oil painting on canvas is preventing canvas from being affected by changes in temperature and humidity. This was the reason for this investigation which resulted in solving the problem of making canvas hydrophobic.

The following requirements were made to the conserving composition:

- (1) the material is to be inert to all the components of a painting;
- (2) the material is to render canvas stably hygroscopic keeping its vapour and air permeability and strength;
- (3) the material is to be convenient for work and non-toxic;
- (4) canvas conservation is not to affect any restoration treatment.

When analyzing the task set, studying researches and references in this field, we came to a conclusion that the only class of materials meeting all the above requirements is the class of organo-silicon compounds.

As is known, organo-silicon moisture barriers do not form a continuous film on the surface of the material processed, do not prevent moisture from evaporating, retain the texture and colour of the surface treated and are physiologically harmless. The compounds have good vapour and air permeability, reduce crime retention of the material treated and, which is most important, render it water-repellent for a long time. Organo-silicon moisture barriers have low surface tension and easily wet textiles with the fibre surface absorbing the compound by filling all the accessible pores and capillaries. The fibre surface is coated by a uniform, flexible, strong and very thin film with an exceptionally high adhesion to the fibre. It was further established that organo-silicon compounds, whose silicon atom, has reactive groups reacting easily with the hydroxyl groups of canvas cellulose resulting in a chemisorbed water-repellent film on the fibre. The hydrophobic properties of the film are ensured by a certain orientation of radicals, the disappearance of part of the cellulose hydroxyl groups, as well as by their screening occurring when three-dimensional structures are formed. The resulting three-dimensional structure prevents the distance between cellulose chains from growing and, consequently, moisture from penetrating between them.

In connection with all the above-said we selected, to conduct comparative experimental investigations, a whole series of moisture barriers that are compounds of two classes: oligoalkylhydrosiloxanes and oligoalkylhydrosilanes.

The initial comparison of materials was made by the resulting hydrophobic effect of the surface determined by the percentage of water adsorption of the treated canvases as compared to the untreated ones.

The concentrations of hydrophobizing compositions tested were in the range 0.5-10%.

The minimal water adsorption by solutions of the same concentration was shown by silanes, and most preferable of these were oligoethyl-oligomethylhydrosilanes since they were applied from such solvents as white-spirit and ethyl alcohol. Water adsorption, after canvas was treated by silanes, was reduced to the value of 25%, of that was absorbed before treatment. Measuring tensile strength showed that the treatment not only does not reduce, but enhances the canvas strength though not substantially, by about 10-12%.

Then the treated and control samples were subjected to accelerated ageing in the hydrostatic chamber for 30 days (at 98% humidity).

dity and 60°C temperature).

As is known, the canvas, artificially aged in the climate chamber, is substantially destroyed which was confirmed by the data obtained by us. Whereas the aged initial canvas lost over 12% of its strength and increased its water adsorption to the same extent, for the canvas after screening the fibre by the treating, these figures constituted from 4 to 0% strength and 6% water adsorption.

After that we studied such properties of the hydrophobized canvas as hygroscopicity, water resistance and contact wetting angle. Comprehensive tests showed a high degree of hydrophobia of the treated surfaces, the durability and reliability of treatment. These canvases do not get wet, quickly yield surface moisture, do not shrink and deform, withstand a sharp rise in humidity with their vapour permeability as high as that of the initial canvases.

The next stage in the investigation was a study of the effect of hydrophobization upon restoration processes.

The painting canvas is subjected to most restoration processes, so its treatment has a direct effect upon their implementation. The determination of the hydrophobization effect upon the process of eliminating rupture by jointing showed that there had been weakening of glueing.

The study of the effect of hydrophobization treatment upon the restoration process of flattening distortions showed that this treatment does not obstruct the process of removing painting canvas distortions. This can be explained by saving of vapour permeability of treated canvas.

The next restoration process, which was considered in connection with hydrophobization, was the process of painting consolidation: As a result of the investigation the following advantages of canvas hydrophobization were found. Normally unprotected canvas fibers quickly absorb the conserving material rendering, subsequently, the author's canvas non-elastic, brittle and causing substantial deformations of the picture. In the case of canvas hydrophobization a reliable barrier is set up against glue composition penetrating the canvas and, what is most important, against it getting to the reverse side of the picture. This prevents the setting up of dangerous stresses in the picture in the course of restoration. This exceptionally significant fact makes possible a qualitatively new level of conservation of oil painting on canvas: restoration without forced lining of pictures with a sufficiently strong original canvas. To avoid lining with glue carried out because of the need for treatment of the original canvas eliminates a complex process which should only be employed in extreme cases where the original canvas is very weak. In addition, a lining canvas often covers autographs, the artist's inscriptions, etc. on the reverse side. And finally, when consolidating pictures on hydrophobized canvas much less glue is used, which is, as was said above, quite favourable for the preservation of pictures.

It was further found that, when it became necessary to line the conserved canvas, its having been treated did not obstruct the procedure. Moreover, it turned out that adhesion of the lining glue to the hydrophobized canvas surface grows approximately 1.5 times; in so doing the amount of glue used to fix the treated canvases was half that of the control samples. That is, canvas hydrophobization was quite favourable for the lining process since the adhesive properties of surfaces become better, glue penetration into the canvas is reduced, it becomes possible to apply the glue composition to the surface just once and, finally, the duration of drying of the glued surface decreases. The treatment of canvas by a moisture barrier can be done both by a brush and pressure spraying. The conservation of fine-grained canvas is best made by spraying. The method of applying the composition should be varied depending upon the desired fibre penetration depth, the condition of the painting and the picture as a whole, and the purpose of treatment itself.

A lot of pictures were restored in various museums and restoration workshops of Moscow, Kiev, Riga, Tallinn and Novgorod by the technique elaborated by us. Thus, pictures were restored, which, by the traditional methods, would inevitably have been lined on a new support. Among them there are, for instance, A.Yermolenko's picture "The Portrait of a Man against Red Background" which had a very crumpled, thin canvas, thin ground and paint layer, the same author's "A Flat Bread Seller" painted on a friable and flimsy canvas, and A.Kozochkin's "Self-Portrait" on a strong, very deformed canvas with rigid cracks. In all these complicated cases the restoration process was rendered substantially easier and simpler. In addition, the author's inscriptions and titles on A.Yermolenko's pictures remained visible.

Another case when hydrophobization substantially facilitated the process is the restoration of B.Kuestodiyev's "On the Volga"

on an oval stretcher. Removing and then stretching the picture back on such a stretcher is a complicated and painstaking job. The employment of hydrophobization made possible a restoration without taking the picture off the stretcher. Canvas hydrophobization process was widely used in Novgorod Museum both for the restoration of pictures and their storage. The pictures were covered by means of a hydrophobized canvas.

Conclusion

In conclusion we note that the canvas hydrophobization method has two aspects: one is restoration and the other, storage of oil painting on canvas.

Bibliography

1. M.Sobolevsky. Properties and using of organosilicon products. M.Chemistry, 1975.
2. N.Zhyravljova. Interaction of oligoethylgidrosilazans and silazans with cellulose fibres. In "Chemical technology of fibre materials". M, MTI, 1973.
3. V.Velcin. Silicons and their application for textiles. M., Gizlegprom, 1968.
4. R.Mille. Silicones. M., Chemistry, 1974.
5. A.Degionskye. Lyophilizing of dispersed system. Kiev, 1960.

ABSTRACT

As part of the training of restorers, a description is given of various possibilities for the treatment of cracks in pictures with synthetic adhesives. The problem is to check which methods for crack treatment can be combined with which adhesives in the case of lining. In doing so, a series of tests was carried out. As a result, recommendations can be given for more or less suited combinations of synthetic adhesives.

The treatment of cracks in canvas paintings with synthetic adhesives - Procedures and possible combinations with the lining process

Ingo Sandner
Academy of Fine Arts
Güntzstraße 34
DDR-8019 Dresden

Synthetic adhesives have opened up new possibilities of painting conservation for the restorer. New methods of bonding, sealing, welding and cramping cracks, new information about the deformation of picture areas, and the development of the low-pressure table have entered the practice of restoration in the last ten years. Lining, once a standard procedure with all torn pictures, is now only justified in more serious cases. The modified use of synthetic adhesives for the treatment of cracks enables torn parts of the picture to be firmly joined together again.

The following materials and methods are chiefly employed at the Department for Restoration of the Dresden Academy of Fine Arts for crack treatment:

Welding:

- Lascaux polyamide textile welding powder (5060 80 °C)
The powder is melted to a thin film between two layers of silicone paper, cut and welded onto the crack with a hot spatula. Spot-bonding is achieved with small sticks (rolled film) and a copper needle fitted into the hot trowel. The tensile strength of the welded crack is increased by melting the powder on a nylon gauze.

Bonding:

- Acrylate dispersions: mixtures of Scopacryl D 343 and D 361 (9:1) or of Plextol D 360 and D 541 (9:1) each with 10 % solids content. This dispersion mixture is applied to the area of the crack in an approximately 5 mm strip, beginning with the torn fibres. When applied to silicone paper, the adhesive dries to form a sealing film or can also be used to coat nylon gauze.
- Acrylate dissolved in toluene or benzine (e.g. Piaflex F 41, LT 30, Plexisol P 550, Paraloid B 72)
A 10 % solution in toluene or benzine is applied, with intermediate drying times, to the area around the crack in the same way as was described for acrylic resin dispersions.
- Polyvinyl butyral, 10 % solution in ethanol
Three coats are applied as described.

Sealing:

- Acrylate sheets
As noted under "Acrylic resin dispersions", sealant sheets are produced either by heating (mixture of Plextol D 360 and D541) or by wetting with a solvent mixture of toluene and white spirit (1:1).
- Hot seal adhesive (Salie 83) /1/
This contact adhesive which was specially developed for lining can also be used for the treatment of cracks when nylon gauze or fleece is used as a reinforcement. The gauze or fleece is coated. The sealing temperature is approximately 63 °C.

Cramping:

Canvas, polyamide and polyester threads may also be coated with hot seal adhesives and acrylate dispersions to cramp cracks. The occasional use of spot-bonding with epoxy resins ensures a higher resistance to solvents, but the torn area is hardened and, thus, susceptible to further marking. All the above-mentioned materials are either soluble or capable of swelling in particular solvents, thus limiting further treatment of the picture.



Painting before and after conservation.
The cracks are bonded with acrylate dispersion.



The large number of new possibilities have broadened our scope of action, enabling us to choose a procedure specially suited to a particular object, but also increasing the danger of damage to the work of art through the use of an inappropriate material. A particularly awkward situation arises when the treatment of the crack proves insufficient, and relining is, indeed, necessary. We have devoted particular attention to this problem in the last two years.

It is worth considering the following questions:

- what is the tensile stress of the material used to seal the cracks?
- how does this stress change with the exposure to solvent (picture cleaning) or heating (lining)?
- which crack treatment adhesives can be combined with which lining adhesives?
- is there a difference in the intensity of the lining bond between the torn area and the rest of the picture?
- how does the intensity of bonding in the torn area respond to solvents or heat?
- does the crack stability remain constant after subsequent lining or does the material used adhere to the relining material more strongly than to the original?

The first two questions are relatively easy to answer. Tensile stress tests on a series of 5 cm wide samples the two fabric parts of which had been either bonded, sealed, welded or cramped yielded at least reference values. All the above-mentioned procedures tend to fail at 5 kg or over but withstand a minimum load of 3 kg on 5 cm, which is usually not exceeded by stretching or climatic conditions even in larger pictures. The load capacity is raised by nylon gauze or fleece reinforcements.

The remaining questions, which arose when lining followed crack treatment, were not so readily answered. Tests were carried out in this problematic area as part of seminar work in collaboration with the Institute for Polymer Technology of Dresden Technical University and with the support of the chair of archaeometry at the Dresden Academy of Fine Arts /2/. The material to be tested was pre-glued, doubly primed canvas with ten incisions each which had been bonded, sealed, welded or cramped according to one of the above-mentioned procedures and was finally relined in four different ways. The adhesives for the selining fabric were hot seal adhesive Salie 83 (Complies roughly with BEVA 371), Plextol D 360, rye flour paste and a wax-resin mixture (2:1). A total of 240 strips, 90 x 14 mm, were tested. The climatic conditions in the test room were 55 % rel. humidity and 22 °C.

Tests:

The bonding strength of the individual linings as well as the differences between the torn area treated with adhesive and the remainder was determined by separating (peeling) the lining fabric from the "original" with the help of a device recording all values in a force-travel graph under defined conditions.

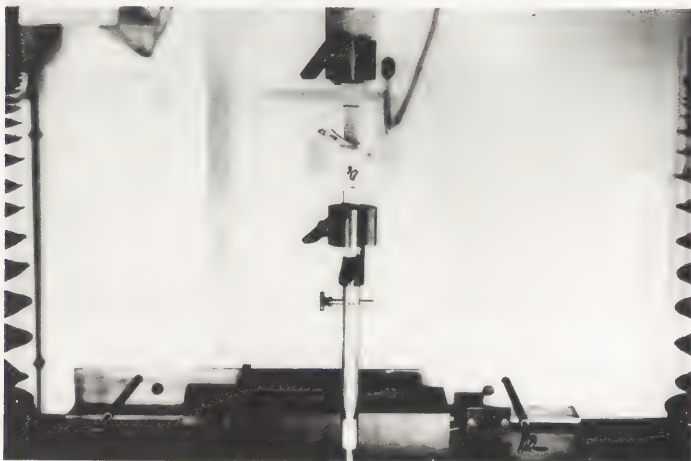
A second series of tests recorded the reaction of the bond to solvents (white spirit, turpentine-alcohol (5:1), acetone, dimethyl formamide and the "reforming mixture"). The mechanically separated hot seal and Plextol bonds were then restuck at approx. 63 °C or 50 °C and their bonding strength was again tested. The evaluation of the travel graph was carried out according to GDR standard 38 387 (Testing of elastomers by means of tearing, separation and peeling trials). So-called medians served as comparable figures.

The aim of the tests was to deduce possible combinations of adhesives for crack treatment and lining. The results should also indicate the disadvantages and dangers incurred in the torn area for the bonds by heat or solvents.

Device recording all values
in a force-travel graph



Tests of the bonding
strength by seperating
(peeling) lining fabric
from the "Original"



The following results were reached:

Hot seal adhesive (Salie 83)

With even coating and an exactly kept sealing temperature, this adhesive achieved a highly adhesive lining, which rose in parts of the torn area, i. e. in connection with the adhesive used. This is particularly evident in crack treatments with an applied acrylate dispersion which is not reinforced with gauze. The bonding to tear sealants with the same hot seal adhesive is also good, though this is disadvantageous in the case of a second lining. Combinations of hot seal adhesive linings and polyvinyl butyral are less suited to crack treatment. The bonding strength is lower. Resticking of the separated samples at a temperature of 63 °C resulted in a higher strength, particularly in the torn area. Thus, there is the undesirable side effect that, after repeated heating, the material used for crack treatment is usually more firmly fixed to the lining material than to the original. When the reinforcing fabric is removed, the cracks are unprotected. This applies particularly to sealing sheets and reinforced gauzes.

The bonding strength is temporarily lowered by solvents. As expected, the torn areas react somewhat more strongly. While the use of white spirit as an adhesive component solvent generally resulted in detachment, the tears treated with polyamide welding powder and acrylates responded to dimethylformamide and reforming mixtures with a marked loss of adhesion to the lining fabric.

Plextol D 360

Here, the adhesion strength is lower than that of the hot seal adhesives (Salie 83/BEVA 371). A reduction in adhesive power is also noticeable after a second heat adhesion process. Plextol bonds tears more firmly which have been treated with acrylate dispersions. All the tested solvents except acetone produced a noticeable weakening of the bond in the torn area after approx. 10 mins. The same tendency to form strong bonds

between acrylates and hot seal adhesives is apparent in tests with Plextol D 360 as with hot seal adhesives. The adhesive clings more firmly to the lining fabric than to the original if reinforced gauze or sheets have been sealed or welded on, if mechanically torn or especially if treated with solvents. If peeling is attempted, cracks appear in the torn area. The only exceptions are the acrylates brush-applied as a dispersion or dissolved in toluene.

Wax-resin mixtures

An even though somewhat low bonding strength is achieved with little difference in the values of the torn area and elsewhere. Sheets which have been sealed or welded on and coated gauzes cause a reduction in adhesion due to their smooth surface.

Rye flour paste

Rye flour paste bonds (admixed with skin glue and Venetian turpentine) showed the highest adhesive intensity of all the tested linings. The adhesive strength between the supporting fabric and the original is usually higher than that between the tested tear bonds. This also includes the gauze-reinforced bonds. Attempts at peeling caused all the tears to reopen. Experience has proved that with time the strength of the paste diminishes to such an extent that this is no longer a cause for concern. More serious is the unmistakable reduction in adhesive power of the lining in the torn area, as the relatively smooth surface of the dried synthetic adhesive or sealing sheet does not facilitate a firm bonding with the paste. In addition, solvents tend to cause detachment in the torn area.

Conclusions

From the experiments it can be seen that the choice of the lining procedure is also dependent on crack treatment. The use of acrylate or polyamide sheets or reinforcing gauzes to raise the tensile stress for non-lined pictures proved to be less suitable for subsequent lining with hot seal adhesives, Plextol D 360 or paste. Either the bonding between the torn area and the lining fabric is too weak, as with paste, or the opposite occurs due to too strong a bonding with the lining adhesive. So the material used to protect the tear comes away when the supporting fabric is removed. Solvents almost always reduce the strength of the bond in the torn area, at least temporarily, and except white spirit and toluene are used for cleaning pictures. Detached linings may be restuck with hot seal adhesive or warmed wax-resin mixtures. Whilst resticking with Plextol D 360 proved disadvantageous.

Paste lining should also include the treatment of tears, remain part of the system and should not be combined with synthetic adhesives. The adhesives do not bond together satisfactorily. If lining is planned from the very beginning, the best method is to coat the damaged area with polyacrylates dispersed or dissolved in toluene, rather than sealing or welding with sheets (polyamide/acrylate) or hot seal bonds with reinforcing gauze, or cramping with laminated threads. Stabilisation of the tear cannot be guaranteed with the use of the latter materials if subsequent heat, mechanical or solvent lining takes place. Of all the tested synthetic materials, polyvinyl butyral appears to be the least suited to crack treatment. The use of the same combination of adhesives for crack treatment and lining is disadvantageous for subsequent lining because, when the supporting fabric is removed, the torn area is left unprotected.

Notes:

- 1 Its properties comply with BEVA 371
- 2 Sack, Ulrike: Kombinationsmöglichkeiten von Rissbehandlung und Dublierung an Leinwandbildern - Testreihen." Seminar project in the specialized field of picture restoration; tutor: Prof. Dr. I. Sandner

Lining

	BEVA Salie	Plextol D 360	wax resin	paste
polyamide welding powder	x	x	x	x ²
acrylate dispersion applied 3 times	x	x	x	0
acrylate in toluene/white spirit	x ¹	x	x	0
acrylate sheets	0	0	0	-
gauze coated with acrylate	0	0	0	-
gauze coated with polyamide	0	0	0	-
hot seal adhesive (BEVA/Salie)	-	x	x	0
threads coated with acrylate	0	x ¹	x	0
threads coated with hot seal adhesive	-	x	x	x
polyvinyl butyral	-	0	0	-

Possible adhesive combinations:

- unsuitable

0 possible

x recommended

x¹ applicable to acrylates with a melting point above that of
Plextol D 360

x² not applicable to polyamide sheets but only to spot welding

RESUME

Il est possible de provoquer et de faire disparaître artificiellement, en quelques jours, la formation de cuvettes dans des structures anciennes de peinture sur toile par sorption, désorption et perméation de vapeur d'eau. Dans le débat théorique sur les causes éventuelles de ces phénomènes, l'auteur fait tout d'abord le point sur le stade actuel des recherches scientifiques avant de développer de nouvelles hypothèses quant à l'origine de telles déformations de surfaces. Il examine les phénomènes d'osmose, les problèmes de surfaces limitrophes et les états de tension intérieure provoqués par la sorption et la désorption de vapeur d'eau. Il examine également le rôle du réseau de craquelures d'âge dans les processus de perméation de vapeur d'eau.

MOTS-CLES

peinture sur toile, formation de cuvettes, sorption, désorption, perméation

Fig. 1: Extrait du film documentaire en 16 mm "Les tableaux respirent". Le mouvement complet dure trente-six heures. L'intervalle entre chaque prise est ici de trois heures.



REFLEXIONS SUR LA FORMATION DE CUVETTES A LA SURFACE DES PEINTURES SUR TOILE

Volker Schaible
Höhere Schule für Gestaltung
Fachklasse für Konservierung
und Restaurierung HFG
Schänzlihalde 31
CH 3000 Bern 25

Introduction

Nous observons souvent le phénomène suivant sur la surface des peintures sur toile : le pourtour des îlots causés par les craquelures d'âge dans la couche picturale se redresse de manière concave. Cette déformation de la surface, couramment appelée formation de "cuvette" (angl. "cupping"), a presque toujours été considérée comme une lésion grave, justifiant la transposition ou le rentoilage, car on redoutait un soulèvement général. De nos jours, ce phénomène est toléré, du moins dans sa phase première, comme un vieillissement naturel. Dans un stade avancé cependant, ce phénomène est traité aujourd'hui par des méthodes tout aussi énergiques d'aplanissement et de refixage sur le support.

L'auteur a réussi à provoquer et à faire disparaître artificiellement en quelques jours une formation de cuvettes dans la couche picturale de fragments anciens de peinture sur toile. Ces mouvements impressionnants ont pu être concentrés sur quelques secondes et sont maintenant visibles dans un film documentaire, grâce à la technique cinématographique en accéléré (fig. 1).

Conditions climatiques du milieu ambiant comme facteurs importants de l'apparition et de la disparition de la formation de cuvettes

Le point de départ des réflexions développées ci-dessous a été l'observation et l'étude du milieu ambiant dans quelques collections de tableaux conservés aussi bien dans des monuments historiques en partie non chauffés que dans des musées ultra-modernes possédant un système de climatisation. En tenant compte des contraintes physiques du bâtiment, du système de chauffage et de climatisation, de précieuses informations sur l'état du climat particulier des peintures sur toile ont pu être glanées durant ces dernières années.¹ D'une manière générale, l'interaction entre un tableau sur toile et son milieu ambiant se présente sous forme de trois situations typiques :

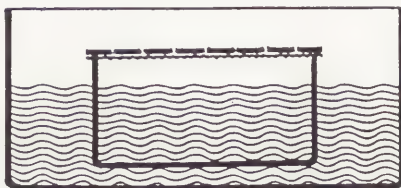
1. Des molécules de vapeur d'eau se trouvant dans l'atmosphère ambiante pénètrent dans la structure du tableau et s'y accumulent. On parle dans ce cas-là d'humidification ou de sorption.
2. Si les molécules de vapeur d'eau quittent la structure et s'évaporent dans l'environnement, on parle d'assèchement ou de désorption.
3. Le terme de perméation implique un transport de vapeur d'eau à travers la structure d'un tableau.

Ces trois situations typiques et toutes leurs variantes ont été reproduites dès 1984 à l'aide d'une installation expérimentale très simple : un petit cadre en verre, sur lequel était fixé un fragment de peinture de 1906 servit de couvercle à un récipient en plexiglas (15 x 10 x 7 cm). Cette chambre climatique, dont le couvercle est formé par l'échantillon de peinture a pu être placée dans un récipient en plexiglas plus grand (35 x 20 x 15 cm), fermé hermétiquement par une vitre. En remplissant l'un ou l'autre ou les deux récipients de silicagel sec ou d'une solution saturée de dihydrophosphate d'ammonium, il fut possible de reproduire toutes les situations climatiques observées dans les collections. La figure 2 montre le dispositif des différents essais. Alors que pour les cas trois et quatre la perméation de molécules de vapeur d'eau (diffusion) à travers la structure de la toile peinte s'est effectuée à une température identique, on a constaté et mesuré un cinquième cas dans les collections de tableaux : une diffusion de vapeur d'eau accélérée par une différence de température derrière et devant le tableau. Il était d'un intérêt particulier que la température à l'intérieur de la structure du tableau descende au-dessous du point de rosée et entraîne la formation d'eau de condensation. Reproduire ces conditions climatiques a nécessité une installation expérimentale plus élaborée.

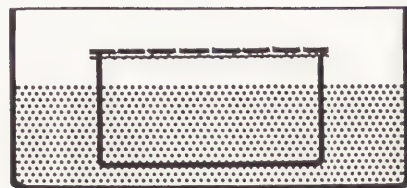
Fig. 1: suite



Fig. 2: Schémas des différents dispositifs d'essais



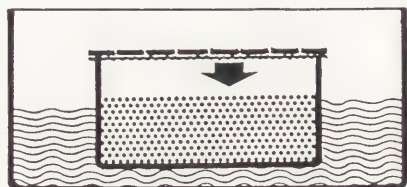
premier cas: sorption (humidification). Les récipients sont remplis de solution saturée de sel. Condition climatique: 20° Celsius (C) pour 96% d'humidité relative (HR).



deuxième cas: désorption (assèchement). Les récipients sont remplis de silica-gel asséché. Condition climatique: 20°C pour environ 4% HR.



troisième cas: perméation (diffusion de vapeur d'eau). Le petit récipient est rempli de solution saturée de sel, le grand de silica-gel asséché. Condition climatique: 20°C avec des gradients de concentration de vapeur d'eau allant de 4% à 96% HR.



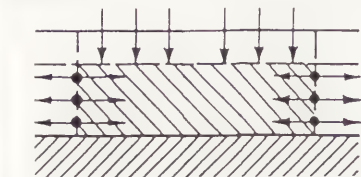
quatrième cas: perméation (diffusion). Le petit récipient est rempli de silica-gel asséché, le grand de solution saturée de sel. Condition climatique: 20°C avec des gradients de concentration de vapeur d'eau allant de 96% à 4% HR.

Au début de cette série d'expériences, il était déjà possible de faire apparaître par des processus de désorption ou disparaître par des processus de sorption, une formation de cuvettes dans la structure des toiles sans trop de difficultés, en leur faisant subir un conditionnement climatique de plusieurs jours (fig. 1). Ces observations n'ont rien de nouveau. L'aplanissement des cuvettes par une humidification de longue durée est exécuté aujourd'hui dans maints ateliers. C'est pourquoi le terme anglais "relaxing process" ou "relaxation treatment" s'est imposé pour définir ce nouveau traitement. Alors qu'autrefois les déformations de la surface d'une peinture sur toile étaient humidifiées pour être aplanies par la suite, elles sont de nos jours "relaxed". La conservation et restauration souffrent de ce que le sens de certains mots se perd de plus en plus dans la langue courante ou que les termes techniques sont souvent employés à tort par manque de connaissance. "To relax" est traduit par relâcher, détendre. On peut alors supposer que lors d'un "relaxation treatment", c'est-à-dire d'une humidification, les tensions internes dans la structure de la toile peinte devraient être abolies. Se forme-t-il pendant ou après la sorption un état libre de toutes tensions, ou au contraire se crée-t-il dans la structure humide un nouvel état de tension ? Le problème est encore loin d'être élucidé. À côté de cela on peut aussi faire allusion avec le terme "relaxation treatment" à la "relaxation", comme terme de base de la mécanique classique de déformation. Il reste cependant totalement incertain que le simple processus d'humidification puisse déclencher un processus de relaxation dans son sens scientifique le plus strict.

Réflexions sur le stade actuel des connaissances

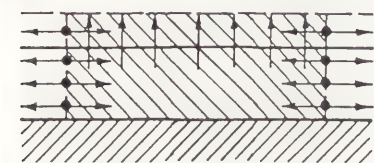
Aussi différemment que puissent se manifester les phénomènes d'altération des peintures sur toile, ceux-ci découlent finalement presque toujours de processus de déformation d'ordre purement mécanique, avec ou sans lésion. Cette relation fut déjà reconnue en 1942 par F.I.G. Rawlings², puis de manière plus aiguë par S. Keck³ en 1969. De plus, le vaste travail de M. Mecklenburg⁴ en 1982 mérite d'être souligné. C'est à G.A. Berger que l'on doit d'avoir la possibilité de mesurer et d'enregistrer les forces mécaniques déformatrices de la structure de la peinture, provoquées par les variations atmosphériques. Il réussit dès 1982 à élaborer avec W.H. Russell des schémas explicatifs de détériorations dues à des états de tensions dans deux dimensions, provoquées par des forces mécaniques⁵.

Fig.3: Diminution de volume



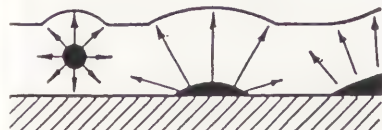
Les diminutions de volume sont provoquées par le dégagement de substances de faible poids moléculaire telles que les produits de dégradation ou par l'agrandissement des molécules lors des réactions chimiques de réticulation. Les contractions thermiques, les processus de désorption et les échanges d'ions peuvent contribuer à ces phénomènes. Les contraintes mécaniques de contraction peuvent également provoquer une lésion.

Fig.4: Augmentation de volume



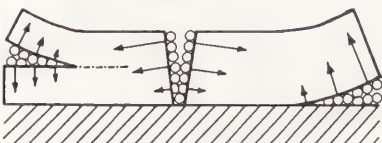
Les augmentations de volume sont provoquées par la dilatation thermique des pellicules, par la sorption et sans doute aussi par des échanges d'ions. Elles peuvent affaiblir les contraintes mécaniques de contraction et provoquer également de nouveaux états de tension.

Fig.5: Processus d'osmose



Les processus d'osmose sont provoqués par l'inhomogénéité de la structure des pellicules polymères, en présence de groupements hydrophiles ou de substances solubles à l'eau (pigments) dans le réseau moléculaire du polymère. Un tableau présente souvent un ensemble de deux couches, constitué d'une couche de préparation aqueuse hydrophile et d'une couche picturale plutôt hydrophobe, situation qui engendre forcément des processus d'osmose. Il en résulte un gradient de pression qui provoque des déformations sous forme de cloques ou de détachement de la pellicule de son support.

Fig.6: Problèmes de surfaces limitrophes



D'autres problèmes peuvent être déclenchés par l'adsorption de substances actives (vapeur d'eau) sur les surfaces limitrophes. Ces substances peuvent influencer l'adhérence des pellicules. L'absorption de substances agressives sur des surfaces limitrophes intérieures telles que des micro-fentes ou pores peut provoquer une ouverture de fissures et accélérer ainsi la formation de lésions.

Les schémas représentatifs bidimensionnels ne suffisent pas cependant à expliquer le phénomène de la formation de cuvettes. Cette hypothèse a pu être confirmée dans une série d'expériences particulières : le même échantillon non tendu, tendu et tendu à l'extrême fut soumis plusieurs fois aux cycles climatiques décrits plus hauts de manière à essayer d'influencer la formation de cuvettes par une traction extérieure. Dans toutes les structures de peintures examinées, les différents états de tension des échantillons n'avaient aucune influence sur l'apparition ou la disparition des cuvettes. Les forces agissant dans la structure du tableau sont donc bien trop fortes pour être neutralisées par des tensions extérieures. Pour exprimer plus clairement le comportement des pellicules sous l'influence de forces extérieures ou intérieures, il faut abandonner les représentations à deux dimensions et se tourner vers une troisième. Cette troisième dimension sous-entend des facteurs nocifs qui déclenchent des réactions chimiques, physiques et physico-chimiques dans la structure d'un tableau. Les mécanismes destructifs sont expliqués dans les schémas (fig. 3-6). Vus sous cet angle les processus de vieillissement d'une manière générale ne sont qu'une fonction des variations de température, des effets de la lumière, de l'action de substances agressives et de la dégradation biologique. Pour mieux comprendre ces données, il ne faut pas perdre de vue que les couches de préparation et de peinture passent de l'état fluide à l'état solide. Les réactions chimiques ne s'arrêtent généralement pas après la formation de cette pellicule solide. Seule la mobilité moléculaire se fige, l'équilibre thermodynamique n'étant pas atteint. Tant qu'il y a encore des zones réactives, la réticulation augmente avec le vieillissement. La structure moléculaire et les conditions ambiantes pendant la polymérisation peuvent entraîner un agrandissement des molécules. Une augmentation de la dureté, de la résistance à l'usure et au gonflement ainsi que d'autres propriétés importantes en découlent qui sont considérées comme une amélioration des propriétés de cette pellicule. Une réticulation trop prononcée entraîne cependant une fragilisation progressive. De légères forces mécaniques suffisent alors à détruire cette pellicule.

Si nous considérons les processus de vieillissement en fonction de ces données comme étant des réactions thermodynamiques destructrices, même les schémas représentatifs tridimensionnels ne suffisent plus pour comprendre la profusion de problèmes qui se posent. Le temps, quatrième dimension particulièrement importante, a été trop longtemps négligé. D'après les déformations de surface que nous avons observées dans nos essais, il semble que l'instant où les facteurs nocifs comme la chaleur, les rayons ultra-violetts, les énergies mécaniques et les substances agressives comme la vapeur d'eau influencent le déroulement des réactions thermodynamiques dans les différentes couches d'un tableau soit d'une grande importance.

Cela démontre que la formation de craquelures et de cuvettes dans les couches de préparation et de peinture peut être également provoquée par des processus de sorption, désorption, perméation de substances agressives comme la vapeur d'eau et par l'action de radiations électromagnétiques, sans que la structure du tableau ne soit tendue. A côté des phénomènes purement physiques d'humidification, de diffusion et de gonflement, se passent simultanément des réactions chimiques qui transforment les macromolécules d'une manière telle que l'on pourrait parler de "corrosion fissurante", par analogie avec la corrosion des métaux.

Action de l'eau et de la vapeur d'eau sur la structure des peintures sur toile

Parmi les influences extérieures existantes, il semble que l'action de l'eau et de la vapeur d'eau soit la plus lourde de conséquences. Il existe beaucoup de publications sur le gonflement des films polymères, cependant les expériences sur le gonflement à proprement parler et sur la localisation de l'eau dans la pellicule gonflée sont récentes. Les nouvelles données nous forcent à moduler notre jugement sur l'action de l'eau et ses conséquences pratiques. Sous le mot gonflement on sous-entend une prise d'humidité homogène par laquelle les polymères ou segments de chaîne sont plus ou moins solvatés mais d'une manière régulière. Il en découle une température de transition vitreuse plus basse et ainsi une plastification des polymères. L'observation d'une absorption homogène d'eau par gonflement est d'abord purement théorique. Dans la pratique un gonflement homogène dépend de deux facteurs importants : la durée d'action de la vapeur d'eau et l'épaisseur du film polymère. H. Klopfer⁶ a publié des résultats intéressants à ce sujet (fig. 7).

Fig. 7: Profondeur de l'action \bar{x} de vapeur d'eau dans les films de polymères organiques.

durée de l'action	profondeur de l'action \bar{x}	
	calculée pour $D=0,15 \cdot 10^{-8}$ (cm ² /s)	calculée pour $D=1,5 \cdot 10^{-8}$ (cm ² /s)
1 seconde	0,0009 mm	0,003 mm
1 minute	0,0067 -	0,021 -
1 heure	0,053 -	0,166 -
1 jour	0,26 -	0,81 -
1 semaine	0,69 -	2,16 -
1 mois	1,42 -	4,5 -
1 an	4,9 -	15,5 -

films relativement imperméables (colonne de gauche) et films relativement perméables (colonne de droite)

par exemple:

huile de lin cuite $D = 0,17 \times 10^{-8}$
 cellulose de méthyle $D = 0,7 \times 10^{-8}$
 huile de lin avec blanc de zinc (25%) $D = 1,31 \times 10^{-8}$

Fig. 8: Evolution des contraintes en surface à coeur au cours d'un essai de sorption.

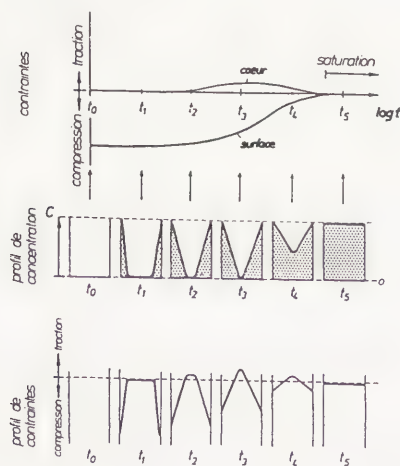
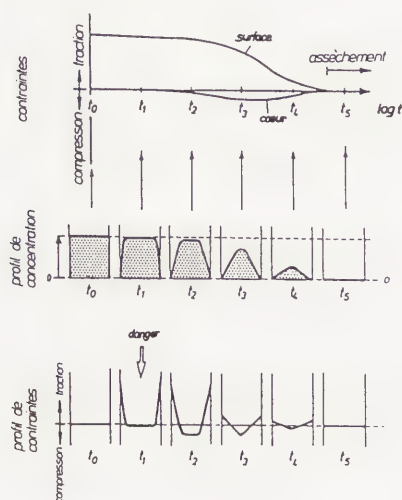


Fig. 9: Evolution des contraintes en surface à coeur au cours d'un essai de désorption.



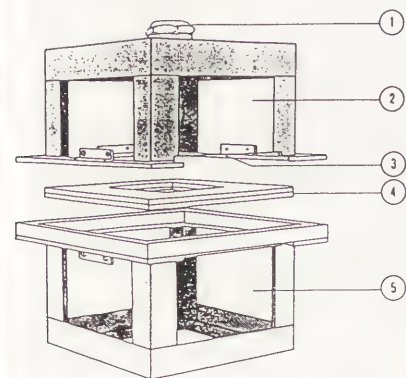
D'après H. Klopfer, la profondeur de la pénétration est relativement importante pour un laps de temps assez court, et suit la loi des racines. Cependant, plus la durée augmente, plus la profondeur de la pénétration diminue. Pendant la phase de solvation, les molécules de vapeur d'eau s'accumulent d'abord à la surface. L'augmentation de volume qui s'ensuit est freinée par les zones internes que l'humidité n'a pas encore atteinte. Il se produit dans toute l'épaisseur de la pellicule des contraintes mécaniques qui se modifient constamment avec la progression de la diffusion jusqu'au point de saturation (voir fig. 8). Elles agissent comme traction au coeur de la pellicule, si celle-ci est humidifiée des deux côtés. Le cas de la désorption se révèle encore plus dangereux. Il s'agit du fait bien connu que l'on peut appliquer à la formation de cuvettes, du sol argileux se desséchant trop vite. Un corps hygroscopique saturé d'humidité qui doit laisser échapper l'humidité par sa surface subit un retrait. Les couches plus profondes et encore saturées l'en empêchent. Il s'ensuit spontanément des contraintes mécaniques dangereuses qui peuvent très vite provoquer des craquelures ou même des formations de cuvettes dans la surface. Les tensions libérées par les processus de désorption sont souvent trois fois plus grandes que celles qui sont dues à l'absorption d'humidité (voir fig. 9). Des réflexions semblables servent de base à la théorie de S. Keck formulée déjà en 1968. Il faut cependant ajouter qu'en réalité il n'existe ni pellicule homogène, ni gonflement homogène. Déjà pendant le séchage d'une couche d'huile de lin sans pigments par exemple, les énergies des surfaces limitrophes provoquent une orientation des molécules à l'intérieur de la couche qui conduit toujours à la formation de trois zones de structure moléculaire différente. En observant une coupe transversale de couche picturale avec un microscope polarisant on voit ces microstructures. Elle apparaissent sous forme d'une membrane extérieure, d'une zone intermédiaire et d'une couche adhérent au support. Si l'on observe à côté de cela un système à plusieurs couches, par exemple un tableau dont la préparation est soluble à l'eau contrairement à la couche picturale, on verra que la vitesse d'absorption d'eau et la quantité de vapeur d'eau absorbée par unité de temps sont extrêmement variables.

Si l'eau traverse la structure et s'emmagine dans les surfaces limitrophes entre pellicules ou entre pellicule et support (fig. 6), l'analyse pondérale de l'augmentation de la quantité d'eau absorbée ne peut plus être mise en relation avec le gonflement au sens propre du terme. Les conséquences de telles rétentions d'eau dans les surfaces limitrophes sont du plus grand intérêt, car elles peuvent vraisemblablement provoquer des pertes d'adhérence, des séparations de couches et même la formation de cloques ou de cuvettes. Dans la littérature spécialisée existent encore des points de vue différents sur les causes de ces rétentions. C'est ainsi que pour certains la rétention d'eau a lieu passivement dans les espaces vides par condensation capillaire. Pour d'autres, cette absorption d'eau à la surface limitrophe s'explique par des processus d'osmose provoqués par la présence de substances solubles dans l'eau, pour lesquels les films polymères agiraient comme membrane semi-perméable ou membrane retardant la perméation. Ce mécanisme est sans doute le plus intéressant pour notre étude. C'est aussi le plus courant puisqu'il se reproduit chaque fois, que ce soit pour une préparation aqueuse ou à l'huile, la toile étant toujours préencollée.

Lorsqu'un tableau est encore jeune et sans craquelures d'âge, il présente une certaine résistance à la diffusion, en fonction des matériaux utilisés et de l'épaisseur de chaque couche de préparation et de peinture. Le tableau s'oppose d'une certaine manière au transport de vapeur d'eau à travers sa structure. Il faut donc se poser la question de savoir dans quelle mesure le réseau de craquelures augmente la perméation. Des essais de diffusion ont été expérimentés sur des échantillons de 10 x 10 cm de toile encollée avec une préparation aqueuse, recouverts d'une peinture à base de résines alkyles, sur lesquels furent pratiquées deux, quatre ou huit craquelures après séchage. Les échantillons ont été soumis à des gradients de concentration de 96 % HR à 53 % HR à 20°C dans un appareil de contrôle, élaboré et construit par M. Kaufmann⁸ (voir fig. 10). Les résultats de ces essais sont représentés dans la figure 11.

Alors que dans toutes les structures de peinture intactes le gradient de concentration n'était pas encore complètement égalisé après 24 heures (courbe a), les essais où l'on avait provoqué des craquelures montrèrent une perméabilité à la vapeur d'eau nettement plus élevée. Avec les échantillons de quatre craquelures (courbe b), de huit craquelures (courbe c), le maximum était déjà atteint après environ six heures, c'est-à-dire que la même quantité de vapeur d'eau traversait la structure endommagée par les

Fig. 10: Schéma de l'appareil de contrôle.



- 1 Raccord pour l'hygromètre électronique
- 2 Chambre climatique du haut conditionnée à 55% HR à l'aide d'une solution saturée de bichromate de sodium
- 3 Tiroir pour le conditionnement de la chambre climatique du haut avant l'essai de perméation
- 4 Cadre de fixation de l'échantillon
- 5 Chambre climatique du bas remplie de solution saturée de dihydrophosphate d'ammonium (96% HR)

craquelures en un tiers du temps. Ce résultat montré très clairement qu'il faut s'attendre à une sorte de "diffusion préférentielle" dans les structures d'un tableau altéré en ce sens que la vapeur d'eau n'a plus besoin de traverser la structure totale de l'échantillon par des processus relativement lents de sorption, perméation et désorption, mais qu'elle peut traverser la structure par les fentes relativement librement. Chaque changement climatique se fait alors sentir immédiatement dans le réseau de craquelures. Seul le pourtour immédiat des craquelures est humidifié lors des processus de sorption de courte durée, alors que la structure générale reste relativement plus sèche.

Pour quelques essais de perméation, l'air de la chambre climatique du bas (voir fig. 10) à 20°C et 96 % HR a été agité sans arrêt par un petit ventilateur. Cela a entraîné l'accélération du passage de la vapeur d'eau. Le maximum était déjà atteint après une à deux heures (courbe d/fig. 11). On peut en déduire que la diffusion de vapeur d'eau à travers les craquelures d'âge d'une peinture sur toile dépend aussi des courants de l'air ambiant.

Ce cas particulier semble être d'un grand intérêt pour le phénomène de formation de cuvettes, puisque justement à l'endroit de la craquelure, l'ensemble des couches se présente en coupe transversale et la vapeur d'eau trouve par là-même un accès immédiat à toutes les couches du tableau. Les processus osmotiques et surtout les problèmes des surfaces limitrophes peuvent ainsi entrer en action, rapidement et librement.

Nouvelles réflexions sur la formation de cuvettes

Si l'on cherche d'autres explications possibles au phénomène de formation de cuvettes dans les peintures sur toile, l'étude publiée par A. Karpowicz en 1989 sur les films de colle de peau de lapin prend une importance particulière. Il a démontré qu'après le séchage, une couche de colle de peau étendue sur un support se rétracte sous l'effet de l'orientation des chaînes de molécules. Un phénomène analogue a été observé lors des processus de désorption: la surface totale ne se rétracte plus mais, au contraire, se détend. Dans cette inversion du comportement hygroscopique habituel de certains liants aqueux, on pourrait trouver une explication très simple au phénomène de formation de cuvettes, de la façon suivante : l'encollement de la toile et/ou les couches de préparation aqueuse d'un tableau jouent un rôle actif en exerçant une compression et une traction sur une couche de peinture plutôt passive. Lors de conditions climatiques normales les couches de peinture d'un tableau ancien sont dures et cassantes et empêchent tout mouvement rapide de gonflement ou de rétraction dans les couches de liants aqueux se situant au-dessous. Ce sont principalement les pellicules de protéines qui absorbent l'humidité très vite et en grande quantité et qui se transforment par là-même en état gélatineux. Si ce processus rapide de gonflement est entravé par la couche picturale durcie se trouvant au-dessus, il se crée des états de tension qui peuvent parfaitement provoquer localement des effets d'orientation dans la structure moléculaire des protéines gélatineuses. Un certain taux d'humidité n'atteint les couches picturales durcies que si celles-ci sont exposées assez longtemps à l'humidité, provoquant ainsi un certain ramollissement des croûtes de peinture. C'est alors que les pellicules protéiniques peuvent provoquer la formation d'une couche picturale ramollie concave en se détendant lors d'un processus de désorption ou peuvent faire disparaître ces cuvettes par un mouvement de rétraction lors d'un processus de sorption.

Cependant, cette interprétation ne semble pas totalement correcte. Une couche picturale ancienne ne se comporte pas entièrement passivement, comme le démontrent les expériences suivantes : des écailles de couche picturale en forme de cuvettes ont été prélevées sur une structure de peinture ancienne. Le dos de ces écailles a été dégagé avec soin de toute particule soluble à l'eau (encollage et préparation). Un séjour de plusieurs jours dans de petites chambres climatiques à 20 °C et 96 % HR a provoqué un léger aplanissement de ces cuvettes. On connaît des effets d'élasticité "entropique" semblables dans la technologie des matières plastiques qui ont déjà trouvé une utilisation pratique dans l'industrie de l'emballage par exemple. Il existe ainsi des revêtements mandrinés, c'est-à-dire des feuilles spéciales qui se rétractent sous l'effet de la chaleur et adhèrent hermétiquement à l'objet à emballer. On parle dans ce cas de capacité de mémoire élastique des thermoplastes ou du soi-disant "memory effect". Il n'est cependant pas encore certain que le phénomène d'élasticité entropique puisse être provoqué également par la sorption de molécules de vapeur d'eau dans la structure des polymères.

A toutes ces interprétations d'ordre mécanique, il faut encore

Fig 11: Représentation schématique des résultats des essais de perméation.

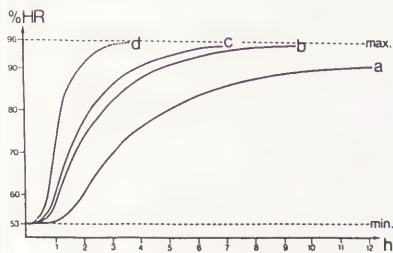
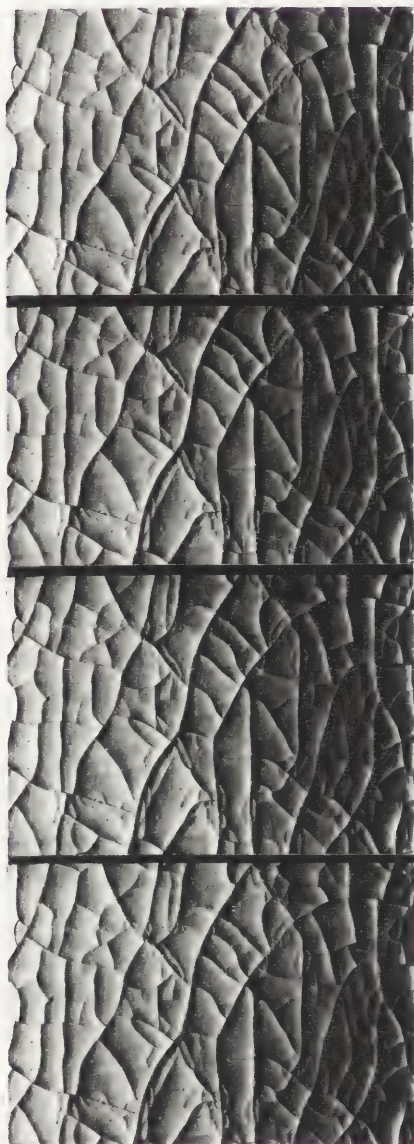


Fig.1: suite



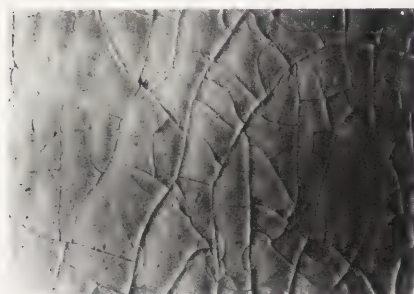
ajouter une dernière observation. Une longue humidification de structures anciennes de peinture (trois à six mois) paralyse tous les mouvements à l'intérieur de la structure. De tels échantillons sont alors inutilisables pour observer des mouvements futurs. Il est encore impossible de définir, au stade actuel de nos connaissances, si seuls des processus de corrosion biologique due à des micro-organismes sont responsables de cette paralysie de la structure ou si nous avons affaire à des processus bien plus compliqués, comme des phénomènes électrocinétiques à l'intérieur de la micro-structure.

Conclusion

Lorsque l'on se penche longuement sur le phénomène de la formation de cuvettes dans les peintures sur toile, l'on remarque très vite l'ampleur du manque de connaissances et de recherche dans ce domaine. Les causes de ce type de vieillissement ont été insuffisamment étudiées jusqu'à nos jours. A ce propos nous pouvons nous demander si nous serons capables un jour de trouver une réponse complète, scientifique et satisfaisante aux phénomènes de vieillissement des peintures sur toile. Ce serait une erreur de ne vouloir considérer ce vaste domaine que sous un angle purement mécanique, purement chimique ou purement physique. Plusieurs possibilités d'interprétation devraient être admises. Pour satisfaire un tant soit peu les exigences scientifiques, le jugement et l'interprétation devraient s'appuyer sur un matériel d'observation très vaste. Nous avons la chance unique d'avoir à notre disposition un matériel d'observation en quantité suffisante. Les musées en regorgent. Cependant, les objets d'art qui s'y trouvent doivent être triés, répertoriés et documentés dans ce but précis. Ce qui n'est pas important doit être éliminé. L'essentiel est à traiter de manière à ce que des théories bien fondées puissent être élaborées et fassent la jonction entre la recherche des causes et le travail pratique de conservation.

Avec la mise en pratique des résultats de recherche, l'élaboration de nouvelles techniques de conservation sur les peintures sur toile devient secondaire. Au stade actuel de nos connaissances il semble que des humidifications de longue durée ne soient pas sans danger et que l'emploi renouvelé de cette technique dans le travail pratique soit un peu prématuré. Bien plus important encore que l'élaboration de nouvelles techniques de conservation semble être l'amélioration des mesures prophylactiques, afin d'éviter la formation de cuvettes sur la surface des tableaux sur toile.

Fig. 1: stade initial en comparaison avec le stade final ci-dessus.



Références:

1. V. Schaible, "Neue Ueberlegungen zur Feuchtigkeit am Leinwandbild", *Zeitschrift für Kunsttechnologie und Konservierung* 1 (1987) 1, 75-94.
2. F.I.G. Rawlins, "The Rheology of Paintings", *Technical Studies* 10 (1941-1942): 59.
3. S. Keck, "Mechanical Alteration of the Paint Film", *Studies in Conservation* 14 (1969): 9-30.
4. M.F. Mecklenburg, "Some Aspects of the Mechanical Behavior of Fabric Supported Paintings" (Manuscript) 1982.
5. G.A. Berger und W.H. Russell, "The New Stress Tests on Canvas Paintings and Some of Their Implications on the Preservation of Paintings" (Preprints of Contributions to the 7th Triennial Meeting of the ICOM-CC, Kopenhagen 1984): 84.2.7.-84.2.9. Dies.: "Untersuchungen zum Einfluss der Umwelt auf die Erhaltung von Leinwandgemälden", *Maltechnik restauro* 95, Nr. 3 (1989): 191-202.
6. H. Klopfer, "Wassertransport durch Diffusion in Feststoffen" (Wiesbaden und Berlin: Bauverlag GmbH, 1974), 139.
7. S. Keck, "Mechanical Alteration", 21
8. M. Kaufmann, "Studien zur Problematik der speziellen Klimasituation am Leinwandbild", (Diplomarbeit, Höhere Schule für Gestaltung Bern, 1988)
9. A. Karpowicz, "In-plane Deformations of Films of Size on Paintings in the Glass Transition Region", *Studies in Conservation* 34, Nr. 2 (1989): 67-74.

ABSTRACT

The painting conservation department of the National Museum of Denmark has devised a transportable suction table for on the spot conservation of large sized paintings.

There are several reasons supporting in situ conservation. Large paintings are normally integrated parts of interior decorations and their conservation must harmonize with the surrounding setting. Additionally, conserving a painting in its accustomed climate would reduce the possibility of traumas. Finally, to transport this type of paintings in and out of a museum atelier, would involve rolling it up on a roller for both, before and after conservation.

KEYWORDS

Suction table, conservation of large sized paintings, conservation of painting on-the-spot.

A TRANSPORTABLE SUCTION TABLE FOR ON-THE-SPOT CONSERVATION OF LARGE SIZED PAINTINGS

Puccio Speroni
National Museum
Bevaringssektion
Brede, 2800 Lyngby
DENMARK

The National Museum of Denmark, apart from its own collections, is responsible for the protection of all works of art under the jurisdiction of the Danish State; that is so to say all the churches, government offices, executive buildings, the Royal Family residences etc. Consequently, all paintings in the above mentioned places, fall under the responsibility of the painting conservation department of the National Museum.

Most of the paintings are of standard size. However, there are a great deal exceeding 10-12 m². These are normally integrated parts of interior decorations and, in most of the cases, ceiling paintings. Conserving this particular type of painting in the the museum's atelier would not only require very large rooms, but would involve dismounting of the painting from its stretcher, rolling it up on a roller and transporting it to the museum. Upon completion of the conservation, the painting would be re-rolled, transported back to its original place and remounted on its stretcher. Understandably, this places enormous stress on the painting and is both a time consuming and costly procedure.

There are two other reasons supporting on the spot conservation. As previously mentioned, almost all these large sized paintings are architectonically integrated parts of ambience and therefore, their completed conservation must harmonize with the surrounding setting. By working in the setting, it is easier to determine, for example, to what extent the painting should be cleaned or what kind of varnish should be used in accordance with the rest of the room.

Climate is the other determinant factor to be considered. The larger the canvas, the proportionately greater will be the reaction to changes in climate. Conserving a painting on the spot, in its accustomed climate, would reduce the possibility of traumas which could have unpredictable consequences.

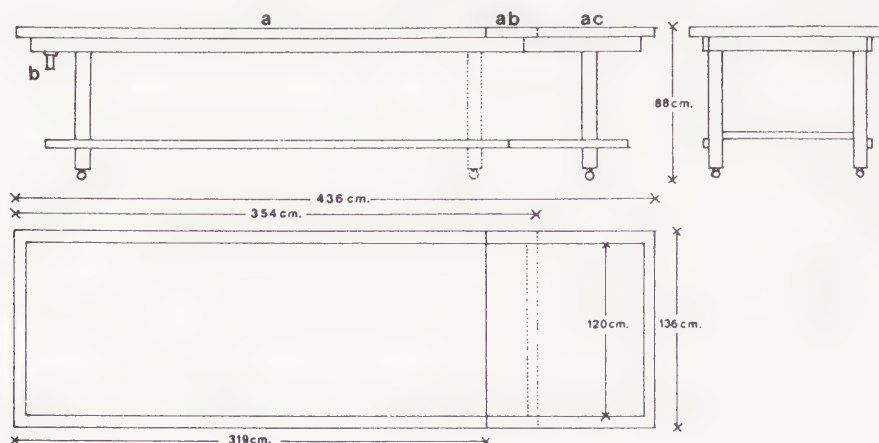


Fig. 1 - The transportable suction table; side views and top view.

a) The fixed module. ab-ac) Two different sized terminals. b) To the aspiration devise.

For these reasons, we have devised a transportable suction table. It enables us to conserve large sized paintings in their natural surrounding. The table is mounted on wheels and measures 136cm. wide, 88cm. high and varies in length from a minimum of 354cm. and on upwards (see fig. 1).

The suction table is made of wood while all the porous materials supporting the aluminium perforated sheet have been selected for their lightness of weight and easy assembly (see figg. 2 and 3)

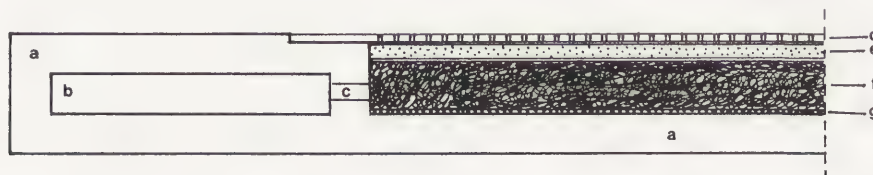


Fig. 2 - Cross section of a side of the suction table.

a) The hollow wooden frame and base. b) Air channel. c) Air suction hole. d) Perforated aluminium sheet, height 1mm. e) Polypropylen felt, height 3,5mm. f) Porous hard supporting material, height 15mm. g) Layer of polyester plain weave fabric, height 0,5mm.

As previously mentioned, the length of the table is variable. This has been necessary in order to conform the suction table to the varying length of the paintings to be conserved. The difference of dimensions is achieved by adding different sized terminals on to the fixed module which measures 319cm. (fig. 3).

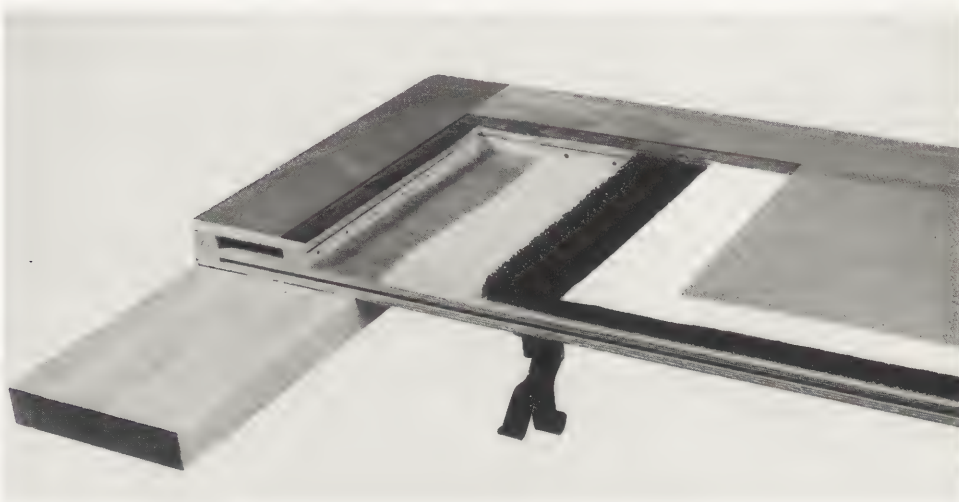


Fig. 3 - Detail of one of the suction table's terminal showing the connecting systems and the different layers of materials supporting the perforated aluminium sheet.

The table is connected to a vacuum cleaner provided with two engines, each of them producing a maximum air aspiration of 55 liter/sec.

The painting to be conserved is stretched by means of extra canvas margins, measuring ca. 25cm. on to a working stretcher, which is then mounted on to a fixed wooden framework measuring 90cm. high. Although in tension, the painting is now free and high enough from the ground allowing the suction table to be moved under it (see fig. 4).

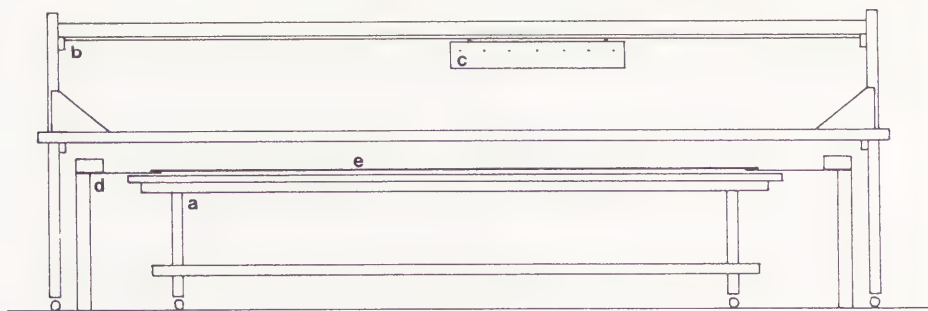


Fig. 4 - Components of the suction table system set together, side view:

- a) The transportable suction table.
- b) The scaffolding with the infra-red ceiling (c).
- d) The framework with the working stretcher.
- e) The painting stretched by means of extra canvas margins to the working stretcher.

The heat source is produced by an infrared ceiling measuring 110cm. x 100cm. This ceiling slides on a rail which is mounted onto a wooden scaffolding. The distance between the infrared tubes and the surface of the painting is measured according to the temperature to be obtained. If all the tubes are turned on at once, the temperature must not exceed 65°C, while the limit is 45°C if alternately turned on. (see fig. 5).

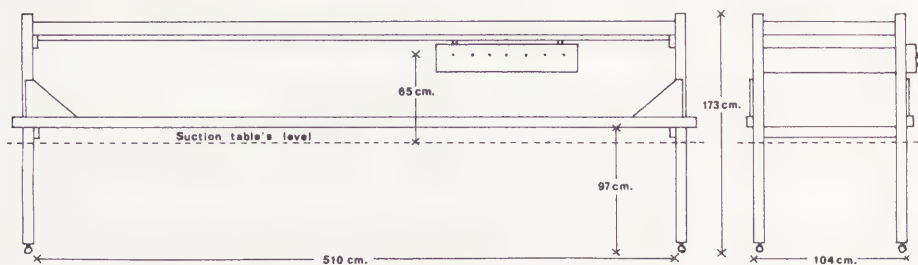


Fig. 5 - The wooden scaffolding with the infrared ceiling (a).

Three large paintings have already been conserved using the on-the-spot transportable suction table method. The structural characteristics of these paintings and condition in general have varied so, requiring that different methodologies and materials be applied. However, in all three cases the outcome of the conservation has been successful.

Materials and Suppliers

Perforated aluminium sheet:

Richard Müller
Industrieparken 40
2750 Ballerup
DENMARK

Polypropylen felt:

Type: Needlana PA-PP/PA 992
Bayerische Wollfilzfabriken KG
D-8875 Offingen
WEST GERMANY

Porous hard supporting materials:

Type: Filtren HC 30
Recticel Deutschland Industrie
5342 Rheinbreitbach
WEST GERMANY

Polyester plain weave fabric:

Type: Polymon PES 25-710 ASTM
Schweizerische Seidengazefabrik
Grütlistrasse 68
CH-8027 Zurich
SWITZERLAND

Vacuum cleaner:

Type: Nilfisk GS 82 with GST engines
Nilfisk A/S
Agenavej 16-18
2670 Greve Strand
DENMARK

References

Falvey, Diane - The Case Study of the Low-Pressure Treatment of a Large-scale Canvas Mural Painting: "The Settlement of Canada" by Frederick S. Haines. In preprints, ICOM Committee for Conservation, 8th Triennial Meeting. Vol. I, pg. 153-159. Sydney 1987.

Hacke, Bent - A Low-Pressure Apparatus for Treatment of Paintings. In preprints, ICOM Committee for Conservation, 5th Triennial Meeting. Vol. I, nr. 78/2/12. Zagreb 1978.

Hacke, Bent - Low-Pressure, Heat, Moisture, Stretcher, Notes on Further Development. In preprints, ICOM Committee for Conservation, 6th Triennial Meeting. Vol. I, nr. 81/2/8. Ottawa 1981.

Leweke, Fritz - Probleme der Restaurierung Grossformatiger Deckengemalde. Bild-träger Leinwand. In: Neue Museumskunde. 1977, nr. 4, pg. 302-310.



Working Group 3

Ethnographic Materials

Matériaux ethnographiques



ABSTRACT

An investigation into the relationship between rate of mould growth and "Aquadhere" PVAc emulsion when used as a binder for traditional mineral pigments in contemporary Australian Aboriginal bark paintings. Experiments revealed that undiluted "Aquadhere" imparted an initial resistance to the painted surface, while upon dilution, (50/50 "Aquadhere/water") the rate of mould growth on the painted surface increased.

KEYWORDS

Fungi; Poly(vinyl acetate) emulsion; Bark painting; Australian Aboriginal.

FUNGI AND ITS RELATIONSHIP WITH ABORIGINAL PAINTED SURFACES CONTAINING THE PVAc EMULSION BINDER "AQUADHERE"

Penelope C. Edmonds
National Centre for Cultural Heritage Science Studies
University of Canberra
PO Box 1
Belconnen ACT
AUSTRALIA

Introduction

Fungal growth on the surface of contemporary Australian Aboriginal bark paintings is a problem which occurs throughout the tropical and humid regions of Australia. Almost all of the painting materials employed by Aboriginal artists are capable of supporting mould, including poly(vinyl acetate) (PVAc) based woodworking adhesives, which are increasingly being substituted for traditional plant-based media.

Presented in this report are the main findings of a study aimed at identifying the relationship between fungal growth and "Aquadhere" PVAc emulsion in its application as a binding medium in contemporary Australian Aboriginal bark paintings. Observations about the quality of "Aquadhere" for use in humid environments are also provided.

1. MATERIALS AND PAINTING TECHNIQUES USED IN CONTEMPORARY BARK PAINTING

In contemporary Arnhem Land paintings, naturally occurring mineral pigments still predominate. Red and yellow pigments are mainly derived from limonite (1). Charcoal and manganese oxide are commonly used for black colourants. The white pigment huntite (almost pure calcium carbonate) is frequently used in the Maningrida region of Arnhem Land, although 'pipe clay', which is predominantly kaolin and gypsum are commonly used in other parts of Arnhem Land.

PVAc wood glue, particularly "Aquadhere" began to replace natural binders in Arnhem Land over fifteen years ago due to its availability, low cost and its ability to be diluted in water. In addition, Aboriginal artists began to recognise the importance of the stability of their paintings for success in the Western market.

The manufacturers of "Aquadhere" state that in addition to the poly(vinyl acetate) homopolymer, "Aquadhere" is comprised of a significant percentage of poly(vinyl alcohol) (PVA1), 88% of which is hydrolysed; a significant percentage of a fugitive plasticiser (coalescent) diethylene glycol mono butyl ether acetate, and a minor percentage of an anionic surfactant described as the sodium salt of a highly sulphated oil. Trace quantities of ammonium sulphate, tartaric acid, hydrogen peroxide, formic acid, sodium acetate and a non-ionic surface active agent are also present.

Analysis of "Aquadhere" was conducted by the author using Energy Dispersive x-ray Analysis (EDXA). Spectra revealed no evidence of trace metals and no chlorine peaks, concluding that "Aquadhere" is organic in composition. The ageing characteristics of "Aquadhere" have been tested by the Australian Museum Conservation Division. (See Appendix 1).

The bark normally used in Arnhem Land is obtained from the stringybark tree (*Eucalyptus tetradonta*). After being cut from the tree, the outer bark is stripped off and the inner bark is dried. Taylor (2) reports that often bark is seasoned by being placed out in 'the weather' and weights are placed on top to aid in flattening. When left to season in this manner, black mould often grows on the surface which must be sanded off before paint is applied.

Pigments are ground with water until the desired consistency is achieved and "Aquadhere" is then added to bind the pigments.

The amount used is dependent on the degree of matt or glossy finish the artist is seeking to achieve.

2. SUSCEPTIBILITY OF BARK PAINTING MATERIALS TO MOULD GROWTH

A review of the literature has indicated that traditional mineral pigments used in Aboriginal bark paintings are capable of supporting mould growth. Rose (3) states that paints containing earth pigments (e.g. sienna, umber, boles) are particularly liable to attack as they are hygroscopic and rich in micro elements. Upsher (4) reports that fungi can utilise vital elements such as carbon, nitrogen and phosphorus as well as trace elements including iron, copper, manganese, molybdenum, zinc, nickel and boron. This is confirmed by Sczcepanowska (5) who, in relation to works of art on paper, states that metallic elements are the most important elements of the nutrient source. Sczcepanowska (5) also comments that many fungi grow very poorly in the absence of iron. Contrary to these findings, a paint film with a high pigment content may also provide initial fungal resistance (6).

The utilisation of kaolin by fungi is doubtful. Studies by Eagon (7) have shown kaolin slurries are greatly resistant to physical change caused by microorganisms.

Dirt and dust on the painted surface of a bark painting can hold moisture and provide a readily available source of nutrients. As the fungi develops it traps more dust and dirt, thus continuing the cycle.

Fungal attack is not related solely to the modern PVAc emulsion binding medium used in a contemporary Aboriginal bark painting. Fungal proliferation is determined by the complementing factors of humidity, pH, availability of nutrients, aeration, illumination and past environmental conditions of the substrate. Furthermore, the susceptibility of pigmented surfaces bound with natural (organic) binding media have been apparent for many years.

The literature has, however, indicated that "Aquadhere" PVAc emulsion, as a material, generally has a low resistance to microbial degradation. Griffin and Mivetchi (8) concluded that polymerised vinyl acetate is clearly capable of being attacked by micro organisms, especially fungi. Upsher (4) suggests that the presence of free acetate may be a reason for PVAc emulsion's susceptibility to mould growth. This may be valid for two reasons: free acetate would be accessible because it is a monomer, i.e. it is not bound up in a chain; and secondly, acetate would provide a ready carbon source. Additives in the wood glue are more likely to be attacked than the base polymer (9). In particular, the plasticiser, diethylene glycol mono butyl ether acetate, although described as fugitive, has been referred to in the literature (10) as having only a moderate resistance to fungal attack. As a major additive, the poly(vinyl alcohol) component of "Aquadhere" may facilitate the crucial moisture content for fungal germination as significant additions of water soluble additives, such as partially hydrolysed grades of poly(vinyl alcohol), can cause the adhesive to be highly sensitive to fluctuations in humidity (11).

"Aquadhere", when used as a binding media for traditional mineral pigments, may provide initial fungal resistance for the following reasons:

Fugitive inhibitors, such as formaldehyde, may temporarily remain in the paint film, causing a fungal inhibiting effect; Although additives are usually quite accessible to fungi, the major constituents of the emulsion including the base polymer, are generally inaccessible. Enzyme attack and chain scission must take place for degradation of the polymer to begin and chain ends are often inaccessible. A synthetic polymer based emulsion, such as "Aquadhere", may be resistant due to its topography upon drying, having a film of a tough, compact and non-porous nature. A paint film consisting of pigments bound with a proportionally high quantity of undiluted "Aquadhere" may initially provide both a moisture and oxygen barrier between the upper surface of the bark and the atmosphere.

Bark, as with wood, has many constituents which provide nutriment for fungi such as cellulose, sugars and oils. Bark, however, has a generally higher percentage of extractives which are known to be fungi-toxic.

3. EXPERIMENTAL

Two experiments are presented. The first was conducted to

determine whether a relationship existed between the presence of "Aquadhere" as a binding medium (for traditional mineral pigment) and rate of mould growth using visual comparative techniques and scanning electron microscopy (SEM). Experiment 2 was conducted to assess fungal growth preferences of traditional mineral pigments bound in a standard 50/50 v/v water/"Aquadhere" dilution.

All bark samples were taken from a prepared, unpainted section of stringybark (*Eucalyptus tetradona*) from the Maningrida region of Arnhem Land. The author may be contacted for further details of experimental procedures.

Experiment 1

Aim: To assess rate of mould growth on samples of painted bark bound with "Aquadhere" as compared with selected controls, using visual comparative techniques and SEM.

Methods and Materials: Standard quantities of white pigment, typical of those used in Aboriginal communities (a mixture of quartz, kaolin, and mica), were bound in "Aquadhere". Controls were of pigment applied with water only, and uncoated Stringybark. Four replicates of each type were prepared.

Samples were air dried for 72 hours and then placed flat (painted surface up) in a humidity chamber having a constant humidity of 97%. This method permitted a mixed flora of fungi to develop on the samples.

Visual examination of the samples was conducted at 9, 14 and 17 days. Examination with the scanning electron microscope was conducted at 9 days.

Assessing fungal intensity:

Visual: The method of assessing fungal intensity visually was adopted from Australian Standard AS 1157.1.1972 (12) according to a reference photograph. Assessment was made on completeness of coverage and density of growth, rather than degree of discolouration. It must be noted, however, that this technique is highly subjective. The fungal intensity rating scale is used as follows:

- 0 = No fungal growth is apparent even under the microscope
- 1 = Fungal growth is hardly visible to the naked eye, but is quite apparent under the microscope
- 2 = Slight growth covering less than 25% of the test surface
- 3 = Medium growth covering less than 25-50% of the test surface
- 4 = Considerable growth covering 50% or more of the test surface
- 5 = Heavy growth covering the entire test surface.

CAUTION: While assessing fungal growth all specimens should be handled carefully as inhalation of spores can be a health hazard.

Scanning Electron Microscopy: Bark samples painted with pigment applied with water and pigment bound in "Aquadhere" were taken from incubation after nine days, and from these samples (3-4mm²) were removed and freeze dried in a vacuum for 3-4 hours at 10⁻² torr for examination by SEM.

Results: After 5 days incubation, pigment samples bound in undiluted "Aquadhere" (i.e. as provided by the manufacturer) had an initial resistance to fungal attack. These samples showed an intensity growth rating of 1, while control samples of bark painted with pigments applied with water and unpainted bark showed ratings of 1 and between 1 and 2 respectively. After 9 and 14 days, fungal growth accelerated until after 25 days complete coverage (intensity rating 5) was common to all samples. At 17 days growth patterns on painted samples had developed differently from those on bark in that fungal growth, though widespread, was far less intense. Examination with the SEM revealed penetration of the "Aquadhere" bound paint samples by hyphae, causing disruption of the painted surface. (See fig. 1).

Experiment 2

Aim: To assess fungal growth preferences for traditional mineral pigments bound with standard binder/water ratio.

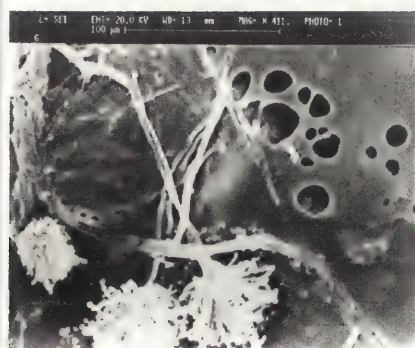


Fig 1 Hyphal penetration through pigment bound in undiluted "Aquadhere" (x411).

Methods and materials: The following four common pigments were selected: Black - ground charcoal;
Red ochre - haematite with a small amount of quartz;
Yellow ochre - goethite or limonite;
White - quartz (dominant), kaolinite (abundant) and mica (small to traces).

Four replicates of each pigment were prepared in the following way: 2mg of pigment mixed in 2ml of "Aquadhere" in water (50/50 v/v) was painted onto the surface of stringybark samples. Other samples included bark coated with a film of undiluted "Aquadhere", bark coated with the diluted binding medium only (i.e. 50/50 v/v "Aquadhere/water"), as well as uncoated bark samples used as controls.

Samples were suspended in sealed glass vessels to which a small amount of water was had been added and incubated for six weeks at a near saturated atmosphere and a temperature of 29 ± 1 . This method was adopted from Kerner-Gang (13). The advantages of suspending the samples rather than placing them on a support, is that fungi can develop freely in both sides of the bark and be easily observed. Two replicate test specimens each were used.

Results: Visual examination was conducted at 2, 4 and 5 weeks. Assessment of fungal growth rate was also made using rating photographs according to the Australian Standard 1157.1.1972.

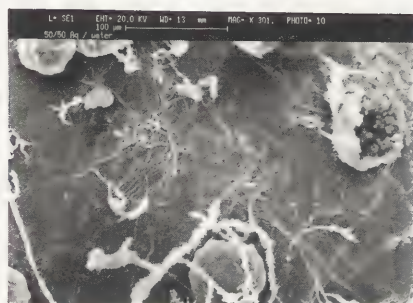


Fig 2 Fungal attack of bark sample coated with diluted "Aquadhere" (50/50 v/v). Note hyphal penetration of surface (x301).

Fungi did not show a preference for the four selected pigments in this experiment, although *Aspergillus* was found on red and yellow ochre paint samples (i.e. those pigments containing iron) which concurs with suggestions made by Sczcepanowska (5) that *Aspergillus* thrive where iron is present. In addition, however, an increase in the rate of mould growth on the painted surface bound in diluted "Aquadhere" (50/50 v/v) compared with unpainted bark controls was observed. At 14 and 17 days paint surfaces of traditional mineral pigments bound in diluted "Aquadhere" (50/50 v/v) showed intensity growth ratings of between 3 and 4, and at 35 days a common growth rating of 5. In contrast, the reverse (unpainted) sides of these samples showed intensity growth ratings of 4 and at 35 days an intensity growth rating of 5. The reverse of these samples also showed significantly less growth. Bark controls had an intensity rating of 2 (slight growth covering less than 25% of the surface) at 14 days and at 35 days a rating of 4 to 5.

Samples coated with undiluted "Aquadhere" had a rating of 1 at 14 days and at 35 days a rating of 2 to 3, showing that undiluted "Aquadhere" did initially resist mould attack, as with Experiment 1.

Examination with scanning electron microscopy revealed hyphal penetration of the diluted "Aquadhere" coating on the surface of the bark. (See fig. 2).

4. DISCUSSION OF RESULTS

Experiment 1 showed that after an initial period of five days resistance to mould growth, painted ochre samples bound in undiluted "Aquadhere" had an increasingly low resistance to mould attack. In contrast to this, Experiment 2 revealed that "Aquadhere", when diluted to 50% water tends to promote fungal growth when used as a binding media with pigments and as a film on the surface of bark, contrary to the behaviour of the undiluted emulsion, observed in both Experiments 1 and 2. Similarly, Experiment 2 showed a coating of undiluted "Aquadhere" on bark to be resistant to mould growth for up to 14 days in incubation.

The results of Experiments 1 and 2 may be combined to draw some conclusions about the behaviour of "Aquadhere" as a binding medium and mould growth in atmospheres of high relative humidity. The trends observed in Experiments 1 and 2 are depicted in the graph (See fig. 3)

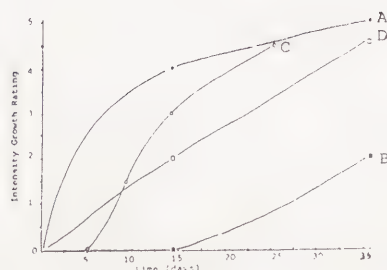


Fig 3 Behavioural trends of "Aquadhere" binder and mould growth.

Trends in the graph indicate that while a binder of diluted "Aquadhere" (50/50 v/v) (A) may exacerbate mould growth under conditions of very high humidity, undiluted as a coating on bark (B) and as a binder for mineral pigments (C) it initially resists mould growth. Bark control samples (D) show a relatively constant rate of mould growth. The results therefore suggest that increased mould growth may be related to dilution

of the binding medium, in high humidity. A specific binder/water ratio may exist where resistance ends and propensity towards mould growth begin. Further research must be conducted to confirm this suggestion. Furthermore, this suggestion should not be considered in isolation; the complementing factors of relative humidity, light, pH, aeration, nutrient sources and past environmental conditions of the painted surface must also be taken into account.

An initial resistance to mould growth may have occurred for reasons outlined in section 2, such as residual formaldehyde in the binder and/or the emulsion's film forming, compact and non-porous nature upon curing.

As increased rate in mould growth, when water has been added to the binder in dilution, may suggest that "Aquadhere" has humectant capabilities, possibly due to the poly(vinyl acetate)'s inherent sensitivity to water and the significant poly(vinyl alcohol) component in the emulsion.

The response of cured "Aquadhere" film to high atmospheric humidity has been explored briefly by the author, where definite physical changes have been shown to occur. (See Appendix 2).

Further research must be conducted to confirm suggestions made in this discussion.

From other sources of information the detrimental qualities of "Aquadhere" as a binding medium are its hygroscopicity, acidity in emulsion form and upon ageing, and instability upon ageing (See Appendix 1). Despite these seemingly adverse characteristics, "Aquadhere" is sympathetic with a bark substrate for its qualities of flexibility, hygroscopicity, chemically organic nature and its permeability to air and water.

In addition, SEM examination revealed that fungal hyphae are able to penetrate both diluted and undiluted "Aquadhere" bound paint samples and cause disruption of the painted surface.

5. CONCLUSIONS

Experiments showed a relationship to exist between dilution of "Aquadhere" PVAc emulsion binder and increase in mould growth. In contrast, when the binder was used undiluted an initial resistance to mould growth was observed.

Generally, while a binder of diluted (50/50 v/v) "Aquadhere" may exacerbate fungal colonisation under conditions of very high relative humidity (possibly due to its humectant capabilities), undiluted "Aquadhere" can at the same time deter fungal colonisation possibly due to its film forming, compact and non-porous nature upon curing and/or residual formaldehyde in the curing adhesive. Further research is necessary to confirm these suggestions.

This information presented on "Aquadhere's" application in contemporary Australian Aboriginal bark paintings together with other information on the quality of "Aquadhere" suggest that a better binding material might be found for this application. Further research on the humectant capabilities of "Aquadhere" is required to confirm these findings.

Much debate exists as to whether the binder is appropriate from a conservation view point, however, "Aquadhere's" continued use as a binding medium in Australian Aboriginal bark paintings is ultimately the decision of Aboriginal artists.

APPENDIX 1:

Testing conducted at the Australian Museum (14) indicated that "Aquadhere" generally was not stable, with a tendency to yellow. Upon accelerated light ageing, changes in tensile properties and solubility were found and differences in ultra-violet visible spectra were produced. In addition, the film extract has pH of approximately 4.0 after ageing. A slightly acidic medium is favourable to spore germination and contributes to the rapid growth of the young colony (5). Both pH extraction tests of Eucalyptus tetradonta bark and "Aquadhere" as a liquid emulsion as well as unaged and aged film extracts have confirmed the acidity of the components of the substrate.

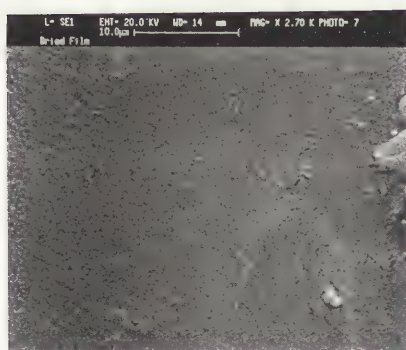


Fig 4 Cured undiluted "Aquadhere" film at ambient relative humidity. Note compact and particulate nature of surface (x2.70).

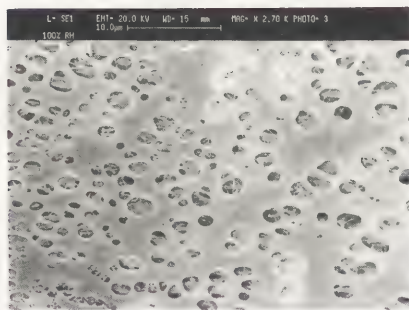


Fig 5 "Aquadhere" film exposed to up to 100% RH. Note porous nature of surface.

APPENDIX 2:

The following exercise was conducted by the author to assess physical changes in cured "Aquadhere" film when exposed to high atmospheric humidity. Scanning electron microscopy was employed for examination. Details of methods and materials for this exercise may be obtained from the author.

At ambient relative humidity the surface of the cured "Aquadhere" film revealed closely packed particles, characteristic of an emulsion upon drying (See fig. 4). After humidification major physical change was observed in the film (See fig. 5). Cavities giving a sponge-like appearance were present. This may be due to the emulsion's sensitivity to water vapour. Further research is necessary to determine the exact process which has occurred upon humidification.

LIST OF FIGURES:

- Figure 1: Hyphal penetration through pigment bound in undiluted "Aquadhere" (x411).
 Figure 2: Fungal attack of bark sample coated with diluted "Aquadhere" (50/50 v/v). Note hyphal penetration of surface (x301).
 Figure 3: Behavioural trends of "Aquadhere" binder and mould growth.
 Figure 4: Cured undiluted "Aquadhere" film at ambient relative humidity. Note compact and particulate nature of surface (x2.70).
 Figure 5: "Aquadhere" film exposed to up to 100% RH. Note porous nature of surface.

1. Duke, C. Pigment Consolidation on Aboriginal Objects, Conservation Double Project, CCAE (1988)
2. Taylor, Luke. Pers. Comm. Australian Institute of Aboriginal Studies, (1989)
3. Rose, A.H. Microbial Deterioration of Material, Academic Press, London, (1981)
4. Upsher, F.J. Microbial Attack on Materials, Materials Research Laboratories, Maribyrong, Victoria (1976)
5. Szczepanowska, H. Biodeterioration of Artworks on Paper, (date of publication unknown) 39-31
6. Gettens, R.J., Pease, M. and Stout, G.L. The Problem of Mould Growth in Paintings in Technical Studies in the Fine Arts, 9(3), (1941), 127-143
7. Eagon, R.G. The Effect of High Microbial Populations on the Physical Properties of Kaolin Slurries in International Biodeterioration vol. 23, (1987), 61-68
8. Griffin, G.J.L. and Mvetchi, H. Biodegradation of Ethylene/vinyl acetate co-polymers in Proceedings of the Third International Biodegradation Symposium, ed. Sharpley, J.M. and Kaplan, A.M., Applied Science Publishers Ltd., London (1976)
9. Potts, J.E. Biodegradation in Aspects of Degradation and Stabilisation of Polymers, Jellinek, H.H.G. (ed.), Elseier, Amsterdam, (1978)
10. Greathouse, Glen A. and Wessel, Carl J. (eds.) Deterioration of Materials: Causes and Preventive Techniques, Reinhold Publishing Corp, Washington D.C. (1954) 544
11. Goulding. Poly(vinyl acetate) Woodworking Adhesives in Adhesives Technology, Marcel Dekker, Inc. USA (date of publication unknown), 345
12. Australian Standard 1157, Part 10-1979, Standard Association of Australia, Standards House, North Sydney, NSW
13. Kerner-Gang. Evaluation Techniques for Resistance of Floor Coverings to Mildew in Biodeterioration Investigation Techniques, ed. A.H. Walters, Applied Science Publishers, London, (date of publication unknown), 95-103
14. Walston, S. and Zounis, S. The Australian Museum Conservation Division

ABSTRACT

A collection of modern Australian Aboriginal painted wooden objects, upon arrival at the Australian Museum were found to be damp and infested with micro-fungi and booklice (Psocids). Tissue paper used to wrap the objects had stuck onto the decorated surfaces. Hyphal filaments also spread across this surface, masking the design. Black mycelium staining was apparent on some of the objects.

Two different types of pigment binder were identified. Acrylic emulsion paints with the binder being a copolymer of butyl acrylate and methyl methacrylate, commonly known as Rhoplex (Primal)(R) AC 235. The second binder used was found to be poly(vinyl acetate) (PVAc), a common wood working adhesive, often mixed with the traditional mineral pigments.

Distilled water was shown to be the most appropriate cleaning solvent in this instance. Further studies into the use of enzymes, such as beta-glucanase and chitinase are being investigated for the removal of the black mycelium staining.

KEYWORDS

Acrylics, poly(vinyl acetate) micro-fungi, mould, stain removal, enzymes.

AN INVESTIGATION INTO CLEANING PROCEDURES FOR MOULD STAINED AUSTRALIAN ABORIGINAL OBJECTS PAINTED WITH MODERN MEDIA

Sue Gatenby
Conservator
Australian Museum
6-8 College Street
Sydney, New South Wales, 2000
Australia

Introduction

A small collection of 7 Australian Aboriginal objects from Papunya and Yuendumu, in the Northern Territory, arrived at the Australian Museum wrapped in tissue paper and exhibited substantial micro-fungal growth. There were signs that these objects had been exposed to a damp environment, with the tissue paper now stuck onto the painted surface. Some objects were newly manufactured and decorated with store bought acrylic paints, with the binder being a co-polymer of butyl acrylate and methyl methacrylate. The other objects were decorated with a paint made by mixing natural mineral pigments and a commercial wood working adhesive, in this case poly(vinyl acetate).

Because the cleaning procedures for these modern materials were unfamiliar to the author, searches were carried out to obtain information concerning their properties. This investigation produced information which will be useful to any conservator who is responsible for the care of similarly decorated surfaces. Although the final cleaning solution is simple, an understanding of the properties of each binder explains why this solution is so successful. This information is presented as Appendices to the treatment outline.

History of Modern Media in the Northern Territory

The Australian Aborigines over the last 70 years have depicted aspects of their cultural and artistic heritage using introduced media painted onto canvas, board and wood. In the 1920's Crayon drawings were produced, with the introduction of acrylic emulsion paints in 1971 (1). Initiated by Geoff Bardon, a young art teacher, painters at Papunya, developed this unique art form.

By the 1980's acrylic painting could be found at several other Central Australian communities including Yuendumu, Mount Allen and Balgo.

Another trend, beginning in the 1960's and seen throughout Central Australia, in response to tourist interest and the need for a more permanent art form, is the use of commercial wood working adhesives. This adhesive is used as the binder and mixed with traditional mineral pigments.

Examination of the Object's Surface

Examination of the fungal growth on the surface revealed that several common micro-fungal species were present, particularly *Penicillium* and *Aspergillus* sp. (These species were identified on the basis of their morphological characteristics).

Booklice were grazing on the microflora, ingesting the fungal spores and hyphae. Booklice being strongly hydrotropic had flourished in the damp environment, depositing their faecal debris, which may be utilized as a nutrient source for the micro-fungi.

Further examination carried out revealed that 4 objects were newly manufactured and painted using acrylic emulsion paints, 2 objects had ochred surfaces only and 1 object had been painted using a mixture of commercial wood working adhesive (either Aquadhere or Mainline) and traditional pigments. This observation was confirmed by the Craft Advisor as well as the Curator who had collected the objects.

Effect of the Micro-fungal Growth on the Painted Surface

According to Upsher (2), there are three basic ways micro-fungi can affect a polymeric material -

(a) if the polymer is susceptible,

- (b) if the polymer is resistant but some other component is susceptible,
- (c) if all components are resistant but the surface deposits or nearby substances are susceptible.

Acrylics and poly(vinyl) resins are known to be resistant to microbial attack. In this case, the secondary constituents of the emulsions although they are in small concentrations, the surface deposits or nearby substances were being selectively utilized rather than the binder i.e. surface dust; tissue paper wrapping; emulsion additives or thickeners such as carboxyl methyl cellulose; or trace elements from the organic pigments.

Dust on the surface of the paintings can provide sufficient organic matter for the initial growth of micro-fungi, under damp conditions. It has also been found that paints containing some earth pigment were particularly liable to attack. They are highly hygroscopic, rich in micro-elements and hence are most frequently subject to micro-fungal growth, compared to paints containing heavy metal ions which are generally resistant.

Aspergillus and *Penicillium* sp. can initially live off dirt or particulate matter trapped in the moisture or condensate on the painted surface. When the fungus becomes established it is able to derive nutrients from other sources. *Penicillium* produces an enormous amount of spores and can rapidly overgrow the material on which they develop. They can cause staining as well as mask the decorated surface.

This kind of biodeterioration is not only one of disfigurement but can also result in failure of a binder. This theory was confirmed to some extent with microscopic examination of each decorated surface. In all cases where excessive growth was apparent, the underlying decorated surface was in a sound condition. Only the acrylics exhibited minor matting of the paint, which was only associated in the areas of black micro-fungal staining.

It has also been suggested by Wolber (3), that the water soluble components such as surfactants, thickeners and plastisizers may have been drawn to the surface of the paint on prolonged contact with moisture, created by the initial damp conditions. This would deliver the possible nutrients to the surface micro-fungal growth as well as produce visual changes such as film matting.

Treatment of the Objects

When the collection arrived at the Museum a routine inspection was undertaken. Immediate action was taken and the collection was fumigated. Fumigation was carried out at a commercial site using Ethylene Oxide (Ethylene oxide: Carbon dioxide 90:10). This fumigation was carried out to prevent further biodeterioration and surface staining of the objects.

Surface Cleaning of the Objects

Loose surface growth was mechanically removed by brushing with a small, pure sable brush and the debris sucked away from the object using a vacuum cleaner. Great care was maintained especially on the unbound surface. An overhead exhaust hood was used to prevent inhalation of the loose matter.

Table 1: Solvent Evaluation for the Removal of the Surface Growth

Solvents tested	Evaluation	
	Acrylic emulsions	PVAc
distilled water	satisfactory	satisfactory
50:50 Ethanol: dist. water	bleeding of red; yellow	fair
5% ammonia	poor	poor
dist. water: non-ionic detergent	good	good
white spirit	softened	poor



Fig 1 Mould stained shield, before treatment.

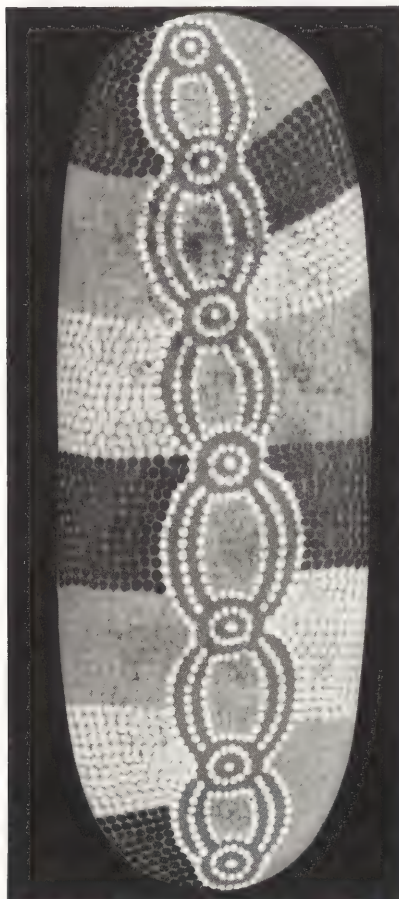


Fig 2 Mould stained shield, after treatment.

As seen in Table 1, the predicted solubilities were demonstrated (refer to Appendices 1, 2, 3). Distilled water was found to be the most suitable solvent. The other alternatives chosen for testing were solvents commonly used for cleaning but their effects on the binder and additives excluded their final selection.

Although each binder is known to be partially soluble in water, this is only after prolonged exposure or immersion. Once the Acrylics are applied to the surface, the water evaporates and the binder fuses to form a continuous film which is water resistant (4). The selection of this cleaning technique is considered suitable and safe, in this instance.

The behaviour of the Acrylic emulsion paints toward the mixture of ethanol and distilled water can be explained by the presence of organic red and yellow pigments, which are known to be susceptible to solvent bleed (refer to Appendix 2).

Various types of facing tissue blotters and poultices were also tested, in combination with the above solvents, but none provided the same successful cleaning results as distilled water swabs.

The next stage of the cleaning was to remove the tissue paper which had stuck onto the surface. This was carried out using moistened cotton wool swabs slightly dampened with distilled water. Blotting of the moistened swab was necessary to remove excess water. The swabs were rolled over the paper which could then be peeled off with the aid of tweezers or a wooden probe. The two objects with ochred surfaces only required the removal of the stuck tissue paper and surface growth was easily brushed off mechanically. They required no further treatment. Further cleaning was necessary for the objects with the 2 different binders, to remove the disfiguring micro-fungal surface growth. These objects were cleaned using distilled water swabs. Again excess was removed by blotting. For heavier staining a drop of non-ionic detergent was added to the distilled water.

Embedded black mycelium staining remained on the acrylic painted objects (Figs 1, 2, 3). This problem would have been exacerbated by the thermoplastic nature of acrylics as well as the period of raised humidity. Alternative cleaning systems (3), such as enzymes are presently being evaluated.

Choice of Enzymes

The cell wall of the hypha of a micro-fungi is complex in both composition and structure. Its exact chemical composition varies dependent on the species. In some fungi there is considerable quantities of cellulose, and in others chitosan and chitin are present to the exclusion of cellulose.

The enzyme selected must be able to breakdown the cell wall of the suspected micro-fungi. Presently, under consideration are 1-3 Beta glucanase and chitinase. These enzymes have been chosen because they are selective to the probable components of the cell wall. Cellulase is considered unsuitable in this case because it can be produced from *Penicillium* and *Aspergillus* sp. Therefore it is understood that these species would have a protective mechanism to prevent enzymatic action upon themselves.

Conclusion

This study provided the opportunity to investigate the modern binding materials used in the preparation of Australian Aboriginal painted objects. Knowledge of the composition and behaviour of each binder as well as pigment characteristics provided essential information for the selection of an appropriate cleaning treatment.

It was found that the micro-fungal growth was easily removed mechanically from the ochred surface. The object painted with the PVAc binder also required swabbing with distilled water as well as mechanical cleaning to remove the surface growth. The acrylic painted surfaces suffered the most damage and exhibited the greatest amount of growth. Mechanical cleaning and swabbing removed all surface growth but further treatment is necessary to reduce the black micro-fungal staining. Both binders exhibited excellent water resistance.



Fig 3 Close up, after treatment results. Note black mycelium staining still present.

Photo Credit.
Ric Bolzan
Australian Museum

The study on the use of enzymes may provide a solution for the disfiguring black staining that remains on the acrylic painted surface.

APPENDIX 1

Properties of Commercial Painting Materials used in Contemporary Art

Acrylic Emulsions

Acrylic emulsions have been available commercially for about 35 years and have been used as an alternative to traditional binders by many artists. According to Lamb (5), important properties of acrylates which should be considered before conservation treatment are:

- (a) Solubility - they are affected by most commonly used solvents.
- (b) Heat sensitivity - they have a low softening point.
- (c) Pressure sensitivity - they have a low softening point.
- (d) Attraction and retention of dirt - dust is attracted due to static charges and can become embedded into the film due to paint film tack.
- (e) Thermoplastic nature - being non conductors static charges can build up which attract dust.

They contain, in addition to the acrylic emulsion, a mixture of glycol, preservatives, wetting agents, pigment extenders, thickeners (usually carboxyl methyl cellulose) and coalescing agents, etc.

Enquiries revealed that the acrylic emulsion paints used in this study were either Atelier(R) or Matisse(R). Technical data indicated that the binder used for these paints was a copolymer of butyl acrylic and methyl methacrylate (commonly known as Rhoplex (Primal)(R) AC 235).

Composition of the Commercial Wood Working Adhesive

Information obtained from the manufacturer of Aquadhere (Selleys).

Commercial wood working adhesives are used as binders and mixed with traditional mineral pigments. The adhesive is primarily composed of poly(vinyl acetate), and a small amount of poly(vinyl alcohol) as well as additives, plasticizers, surfactants, emulsifiers, etc. The solids content of each component varies according to the quality of the adhesive, but approximate concentrations of Aquadhere are presently estimated at 85% poly(vinyl acetate); 10% poly(vinyl alcohol); with 5% other. Another name brand known to be used is Mainline(R), with approximately the same constituents.

APPENDIX 2

Organic and Inorganic Pigments used in the Manufacture of Acrylic Paints

Reported pigments used in the production of acrylic paints (Technical Data obtained from each company) were found to be a variety of organic and inorganic pigments, such as -

Table 2: Pigments used in Acrylic paint formulations

Colour	Inorganic pigment	Organic pigment
Yellow	Chrome Cadmium Iron oxide	Nickel azo Hunza
Red	Cadmium Iron oxide	Quinacridone Arylide
Orange	Cadmium Chrome	Dinitraniline
Blue	Ultramarine	Phthalocyanine
Green	Chromium oxide	Phthalocyanine
Black	Iron oxide	Carbon

Conservation considerations for organic and inorganic pigments are -

- (a) Organic pigments tend to have less resistance to light.
- (b) Organic pigments have variable resistance to solvent bleed, red and yellow are particularly susceptible compared to inorganic pigments which have excellent resistance. (This is an important consideration when choosing a solvent for cleaning).
- (c) Organic pigments have variable resistance to chemicals as well as variable thermal stability compared to inorganic pigments which have a better resistance to each parameter.

There are also variations in colour brightness, tinting strength, opacity and ease of dispersion (6, 7).

APPENDIX 3

Reported Solubility of Binders

Listed below are some reported solubilities (8), of the two binders:

Table 3: Reported Solubilities of binders

Type	Soluble	Insoluble
Acrylic emulsion	hydrocarbons aromatics halogenated hydrocarbons esters, ketones	water*, alcohols phenols ether carbon tetrachloride
Poly(vinyl acetate)	ketones, lower alcohols, aromatic and chlorinated hydrocarbons	water#, petroleum hydrocarbons, dilute acids and alkalis

* Acrylic emulsions vary in solubility but may be slightly soluble in water, however only after prolonged immersion. Water solubility is due to the small amount of water soluble thickening agents found in emulsions, the most common one being carboxyl methyl cellulose. Acrylics are generally considered to have excellent water resistance.

Poly(vinyl acetate) is known to be partially soluble in water, however only after prolonged immersion. This solubility is due to the poly(vinyl alcohol) (PVAL) portion, added as a stabiliser. Different grades and brands will have different amounts of PVAL and hence variable water resistance. Also the thickener, carboxyl methyl cellulose, (CMC), will also contribute to the water solubility.

APPENDIX 4

Particle Sizes of Organic and Inorganic Pigments

Organic inorganic pigments have different particle size ranges (7), i.e.

Particle Size: 0.01 - 1.0 μm Organic pigments
0.2 - 25 μm Inorganic pigments

Particle size plays an important role in the performance characteristics of emulsions. Fine particle size gives a better pigment binding power, hence a higher Critical Pigment Volume Concentration (CPVC), as well as producing a tightly packed film.

It is important to be aware that the two classes of pigment types may be present on the same painted surface. Their different properties and behaviour are significant in the selection of appropriate treatment procedures. Spot tests can be carried out to determine whether a pigment is susceptible to bleeding and identification of the pigment type can be carried out using colour reactions such as those described by Keijzer (9).

Notes

1. Anderson, J.C. Yuendumu: paintings out of the desert. Anthropology Society of South Australia Journal. 1988. 26(1): p 6-11.
2. Upsher, F.J. Microbial Attack on Materials. Proceedings of the Royal Australian Chemical Institute. 1976. p 173-176.
3. Wolbers, R. Art Conservation Program. University of Delaware, Newark, Delaware. (Personal communication), 1989.
4. French, A. Modern Day Artist Colours. Modern Art: The restoration and techniques of modern paper and paints. Proceedings of the Joint Conference of the United Kingdom Institute of Conservation and the Museum of London. 1989. p 21-22.
5. Lamb, C. Acrylics, New Material, New Problems. The Conservation of Modern Paintings: Introductory notes on papers from the United Kingdom, Institute of Conservation, Symposium. 1982. 4 pages.
6. Martens, C.R. Waterborne Coatings. Emulsion and Water-soluble Paints. (New York: Van Nostrand Reinhold Company, 1981). p 115-137.
7. Oil and Colour Chemist's Association, Australia. Surface Coatings. Volume 1. Raw Materials and their usage. (TAFE Educational Books, New South Wales University Press Limited). 1983. p 288-304, 313-343.
8. Roff, W.J., Scott, J.R. Fibres, Films, Plastics and Rubbers. A Handbook of Common Polymers. (London, Butterworths, 1971). p 66-72, 87-99.
9. Keijzer, de M. The Colourful Twentieth Century. Modern Art: The restoration and techniques of modern paper and paints. Proceedings of the Joint Conference, United Kingdom Institute of Conservation and the Museum of London. 1989. p 13-20.

Materials

Atelier Impasto Artists Acrylics(R), Chroma Acrylics (NSW) Pty. Ltd., P.O. Box 3B, Mount Kuring-gai NSW 2080. Australia.

Matisse Professional Artists' Acrylic Colour(R), Vynol Derivan Pty. Ltd., 1 Northcote Road, Mortlake NSW 2137. Australia.

Rhoplex ((PRIMAL) AC 235(R), Rohm and Haas Australia Pty. Ltd., 60 Perry Street, Matraville NSW 2046, Australia.

Selleys Aquadhere(R), Selleys, Chemical Company Pty. Ltd., 1 Gow Street, Padstow NSW 2211. Australia.

Acknowledgements

I would like to thank David Horton-James, Materials Conservation Division, Australian Museum for his advice and support toward this project.

ABSTRACT

Problems encountered in the consolidation of paint on ethnographic wood objects are reviewed, based upon the literature and surveys of North American ethnographic conservators. Significant consolidation may require a large quantity of resin, which will affect the appearance of the paint. Changes in appearance may be minimized by selecting either particular application procedures or resins that are effective in lower concentrations. The solution properties (volatility, viscosity, surface tension) may be as important as, or more important than, the physical properties of the dried resin. As removal of a resin used to consolidate a fragile deteriorated paint is unlikely, the aging characteristics are of primary importance in the choice of a resin. Insoluble thermosetting resins (diisocyanates, epoxies) are considered due to their high strength in low concentrations, compared to thermoplastic resins.

KEYWORDS

Ethnographic, wood objects, paint, pigment volume concentration (PVC), consolidation, aging, resin, viscosity, volatility, wetting, thermoset.

A REVIEW OF PROBLEMS ENCOUNTERED IN THE CONSOLIDATION OF PAINT ON ETHNOGRAPHIC WOOD OBJECTS AND POTENTIAL REMEDIES

Eric F. Hansen*, Eileen T. Sadoff and Rosa Lowinger
The Getty Conservation Institute
4503B Glencoe Avenue
Marina del Rey, CA 90292, U.S.A

*Author to whom correspondence should be addressed.

Introduction

The conservation of many painted ethnographic wood objects is difficult because powdering, crumbling or flaking and porous paint tends to darken or discolor if consolidated with an organic resin. It is doubtful that a consolidant can be successfully removed from a very fragile or deteriorated paint, even if the resin itself can be resolubilized. Therefore, resins used as consolidants are not necessarily required to be resolvable in the future. However, they are required to be particularly stable in terms of future strength and color retention in comparison to picture varnishes or protective polymeric coatings for metals, where future removal is possible.

One major problem with the consolidation of these objects is that often the paint has a high pigment volume concentration (PVC). It has been shown that darkening or discoloration may result by adding a resin to a high PVC paint.(1) Although it is desired that a treatment results in no discernable change in the appearance of an object, conservators must consider the physical limitations of a situation. In many cases where any addition of a consolidant will cause a change in appearance, the desired result will be the minimal amount of change in appearance for the required degree of consolidation.

The purpose of this paper is to provide a summary of available knowledge on the practical and theoretical factors affecting consolidation of painted ethnographic wood objects. To the authors' knowledge, no such summary exists. The information presented here is based upon a review of the existing anthropological, chemical, coating and conservation literature; and the responses to mailed questionnaires and personally conducted surveys of ethnographic conservators in the United States. It will be incorporated into one of the first courses to be offered on the subject.(2)

Properties of painted ethnographic wood objects

Oceanic and African artifacts with natural binders or no binders at all are representative of the most problematic ethnographic painted objects. More recent Oceanic and African objects produced specifically for tourism, and made with commercial paints, wood glue or other manufactured adhesives as binders(3) rarely require consolidation.

Although a variety of mineral and organic pigments were used, the most common are charcoal, red and yellow iron oxides (ochres) and kaolin.(4) The application process varied from one culture to another, but generally dry or wet clay or pigment was applied to a plain wood substrate or wood covered with a resin or a wet gum. A clay or ochre layer was then applied to the surface, but sometimes the natural color of the wood itself was used as the ground color. The ground was then covered with several paint layers to complete the design. These paints would be mixed primarily with water, with vegetable binders, or possibly with animal fats or oils.

Several factors are apparent in this method of painting which affect both the deterioration of the artifact and add to the difficulty in treatment. Future problems will be encountered as the wood dimensions fluctuate with changes in relative humidity. The inflexible paint then flakes. In addition, the paint itself has considerable inherent vice because little or no resin is in the void spaces between the pigment particles. Therefore, the painted surface will have a very high pigment volume concentration (PVC), defined as the ratio of pigment volume to binder volume. In this case, light is scattered from the interface of air and pigment particles. Feller and Kunz have shown that addition of a resin to a high PVC paint causes a darkening effect, due to filling of the void spaces.(5)

The degree of consolidation in this type of paint is related to the amount of resin added; and, the degree of darkening, or loss of diffuse reflectance, is also a function of the amount of

Table 1. Aging Characteristics of Organic Soluble Resins

Class A Materials
Acryloid B72
Poly(vinyl acetate)
Class B Materials
Ethylene(vinyl acetate)
Poly(vinyl butyral)
Class C Materials
<u>Cellulose ethers</u> hydroxyethyl cellulose hydroxypropyl cellulose ethylcellulose organic-soluble ethylhydroxy- ethylcellulose

Table 2. Aging Characteristics of Water Soluble Resins

Class A Materials
Emulsions and cellulose ethers, tested commercial products
Class B Materials
Emulsions (may be class A, B or C, dependent upon the manufacturer)
<u>Cellulose ethers</u> (may be class A, dependent upon the manufacturer) methyl cellulose carboxy methyl cellulose water-soluble ethylhydroxy- ethylcellulose
Gelatin
Class C Materials
Poly(vinyl alcohol)

resin added. Thus, no matter what resin is chosen for treatment, some effect must result on the optical properties of the paint. In addition, the degree of darkening will depend upon the ratio of void spaces to solid particles in the paint layer. Paint with a high fraction of voids may discolor less for a given amount of resin than a paint with a lower fraction of voids.

Another cause of darkening is the loss of diffuse reflectance as a result of coating the surface of the paint. The original artifact could have had a more glossy surface which became more diffusely reflectant as the binder deteriorated or the surface cracked. If the added resin remains on the surface darkening will result, not only from reduced scattering but also from the reduction of diffuse surface reflection.(6)

The diverse cultures of Oceania and Africa used a wide variety of organic binders obtained from local plants and animals, and the binders vary as these species vary geographically. These binders may be partially soluble in organic or water based solutions used to apply consolidants, resulting in discoloration of the paint. Organic pigments, such as tumeric(7) or powdered camwood bark(8) have also been used and, in the case of camwood, may be practically indistinguishable from ochre by visual inspection. These pigments discolor by the action of organic solvents. Solvents may also dissolve resins remaining in the wood and, if brought to the surface, cause further discoloration.

Concerns that affect the choice of materials and methods

Prior to selecting materials and methods of application, the conservator must determine whether the object as a whole is best preserved by intervention. Among the questions that need to be asked are: Where is the object located? Is it exhibited with its painted surface in a vertical position? Is it possible to control climatic conditions or, will the piece endure future fluctuations in temperature and relative humidity? Is the piece part of a study collection which may be chosen for technological analysis at some time in the future? Is it frequently handled by scholars or private collectors? Is it possible to store the object horizontally so that gravity and/or abrasion will not add to the problems?

The answers to some of these questions may direct the conservator to refrain from consolidation. There may be the option of environmentally controlled storage. If not, then the required strength of consolidation must be weighed against acceptable limits to unavoidable changes in appearance. A conscious decision to accept a certain degree of change in the appearance of an object is a serious problem in the conservation of ethnographic painted objects that deserves much discussion and examination, because readily available solutions to this problem are few and the number of artifacts requiring consolidation is considerable.

Properties of dried resins.

A primary consideration in the choice of a resin is the stability of the resin, or resistance to chemical or physical modifications with time (aging). The resins in Table 1 and 2 are currently in use by conservators for the consolidation of painted ethnographic wood objects. They were determined from the response to an in-depth written questionnaire sent to a limited group of 14 ethnographic conservators and from a survey of 80 conservators who were listed as members of the Ethnographic Objects specialty group of the American Institute for the Conservation of Historic and Cultural Works of Art (AIC).

As an object may be susceptible to either aqueous or organic solvents (or possibly both), the resins are broken into two tables based upon their solubility. The resins are classified into three sets in the tables, modeled upon suggestions made by Feller concerning standards for the evaluation of thermoplastic resins.(9) The divisions are made with the following considerations:

1. Class A materials are expected to last in excess of 100 years in a museum environment with less than 20% change in the properties of interest; Class B 20 to 100 years; and Class C less than 20 years. Materials in Class C are considered to be too unstable for museum use.
2. Materials which may last 100 years in a museum environment, but have not been thoroughly tested and of proven stability we have placed here in class B. This particular consideration was not used as a basis for classification by Feller in 1978.
3. Aging characteristics may vary according to manufacturer, this being especially true for the cellulose ethers and emulsions which have a variety of additives (stabilizers,

fungicides, surfactants).

4. Aging characteristics may vary according to the system, i.e. the classification is for the intrinsic stability of the material as tested in a laboratory, and not necessarily functioning as a consolidant or an adhesive.

The initial laboratory-based criterion that Feller used was the photochemical stability of resins and polymers based upon their tendency to cross-link and thereby lose solubility. (In subsequent tests, thermal discoloration and loss of molecular weight were also used as criteria.)(10) However, retention of a certain solubility is not an important criterion for a consolidant of the paint encountered on ethnographic wood objects. In this table, the color stability of Acryloid B72, poly(vinyl acetate) (PVAC) and some of the cellulose ethers is an important consideration. The Class A materials are not expected to discolor appreciably for at least a 100 year time span under museum conditions.

Gelatin, the only natural product included, is considered a Class B material even though under the right climatic conditions (low, stable relative humidity) the material may last several hundred years. Particularly humid conditions favor biodeterioration. The inclusion of poly(vinyl butyral), (PVB), in class B is based upon the second consideration in making the divisions. This material may prove to be a class A material, but to date a definitive study of the aging characteristics is not available. Poly(vinyl alcohol), a class C material, is rarely used but is included in the table because a few of the conservators surveyed mentioned its use. The many available emulsions, which can be composed of acrylic polymers, PVAC and/or PVB, must be considered in the light of comparative testing of manufacturers products. The cellulose ethers have been determined by Feller to fall into two classes of stability: the water-soluble cellulose ethers are not expected to yellow, but the organic soluble have generally been classified as unstable.(11) Therefore, caution is indicated with the use of the latter class of resins.

Refractive index is a property of secondary importance because the optical properties of a high PVC paint change according to the volume of resin added. Where interactions with resins are important, and the PVC is comparatively very low, there may be some concern for the effects of different refractive indexes. Feller personally believes that refractive index rarely needs to be considered.(12) In order to gain an accurate comparison of materials, the degree of consolidation and severity of appearance change must be determined for similar amounts of resins, a task not easy to accomplish. Feller and Kunz have suggested that when very little darkening results from the addition of a vehicle, analysis of the paint will show that the resultant paint is still at a high PVC.(13)

When PVAC has been used as a consolidant in a sufficient quantity, the result was often a visually noticeable film (seen as streaking, darkening and glossiness). The other materials on the list, which are not of the proven stability of Acryloid B72 and PVAC, apparently are being used because these negative effects are reduced. However, we believe the effects on the appearance properties result primarily from the nature of the solution and paint interactions during application, and may not necessarily be dependent upon any particular properties of the dried resin.

Potential remedies resulting from properties of solutions.

The benefits and drawbacks of methods for minimizing appearance changes resulting from attempts at consolidation are listed in Table 3. Some methods depend upon the control of penetration of the paint by solutions of resins, either by using high viscosity solutions to reduce penetration or by using low viscosity solutions to maximize penetration. Also important is the wetting ability of the solutions, when penetration of the paint is hampered by inadequate wetting of pigment particles.

Solutions can be applied by spray or brush, but spraying is often not possible due to the powdering nature of the paint or the close proximity of one or more different pigments. If the paint is flaking, resins can be applied under the surface of the flake by syringe; by inserting a micro-spatula under the lifting surface(14); or by inserting a cast, solid resin which is reactivated by solvent or heat.(15) High viscosity solutions or high resin/solvent ratios are indicated when the solution is applied under a flake and it is desired that the material not spread through the porous media. High resin/solvent ratio

Table 3. Benefits and drawbacks of materials and methods used to minimize changes in appearance.

<p><u>High viscosity solution</u></p> <p>Matte or semi-matte surface retained through lack of penetration and leveling</p> <p>Surface consolidation without improving adhesion to substrate</p>
<p><u>Low volatility solvent (Diethylbenzene)</u></p> <p>Matte surface retained by improved penetration</p> <p>Limited range of soluble resins</p> <p>Long solvent retention</p>
<p><u>Solvent vapor saturated atmosphere</u></p> <p>Matte surface retained by improved penetration</p> <p>Large range of solvents and resins may be used</p> <p>Objects may have solvent sensitive areas</p>
<p><u>Surfactants</u></p> <p>May improve penetration</p> <p>May be useful for soiled, oily paint</p> <p>Available for both organic and aqueous systems</p> <p>Surfactants may adversely affect aging of resin</p>
<p><u>Matting agents</u></p> <p>Decrease gloss of resins remaining on surface</p> <p>Difficult to match color and gloss</p>
<p><u>Thermosetting resins</u></p> <p>High strength may allow use of minimal amount in comparison with thermoplastic resins</p> <p>In situ setting reduces internal stress</p> <p>May be applied in a vapor saturated atmosphere</p> <p>Insoluble</p> <p>Epoxies may yellow</p>

emulsions and the intrinsically viscous solutions that are encountered with gelatin and the cellulose ethers make them particularly suitable for this use.

High viscosity solutions may also be useful when it is only necessary to consolidate the surface without increased adherence to the substrate. If a coating was not able to level itself because of the high viscosity of the applied solution, a matte or semi-matte surface may be formed. Spraying with a highly volatile solvent will increase the viscosity of the polymer solution that reaches the surface.(16) This method may be particularly suitable for treating paint that is matte due to surface roughness or cracking.

For a porous paint that is light and matte due to scattering from pigment particles, such as high PVC paint, maximum penetration is achieved with a consolidant solution of low viscosity. A low viscosity can be maintained by using a solvent of low volatility, allowing maximum time for penetration. Diethylbenzene, a low volatility solvent suggested by Welsh,(17) may be used successfully to avoid a noticeable, sharp interface between consolidated areas and untreated areas, along with retention of a matte appearance. But, because the solvent diffusion in resins is slow for large irregularly shaped molecules like diethylbenzene(DEB) resulting in long-term solvent retention, there is a greater possibility for interaction between organic components of a paint and the solvent. The noxious properties of DEB can persist for an unwanted time period. There is also a limited range of resins that can be used (although Acryloid B72 will dissolve in DEB, other polymers such as PVAC will not).

Multiple applications of a dilute solution may penetrate further than one application of a more concentrated and, therefore, more viscous solution.(18) Another method for maintaining a low viscosity, suggested by Wicks, is to apply the solution in an atmosphere saturated with vapor of the solvent used to dissolve the resin.(19) Faster evaporating solvents may be used successfully because in a saturated atmosphere the solution concentration does not increase rapidly, therefore the viscosity remains constant and the penetration is more effective. The object is treated in an enclosed container which holds pools of solvent, left to remain until penetration is complete, and then removed and the solvent allowed to evaporate. We have had some success with this method in the consolidation of ochres and kaolin with Acryloid B72 in acetone and PVAC in either acetone or ethanol.(20) This method may be restricted to objects, or areas of objects, that are not sensitive to solvent vapors. This method is not restricted in the range of useful resins as is DEB, and can be used when a softer and more flexible polymer, such as PVAC, is preferable to Acryloid B72.

Penetration is also reduced when there is improper wetting of a substrate, such as when an aqueous system is used to consolidate paint that has been formulated with waxes or oils, or has subsequently been soiled with oils. The wetting ability of solutions can often be improved through the use of surfactants. Surfactants modify the interfacial surface tension of a liquid, i.e. in this case, the energy at the interface of the liquid and solid pigment particles is reduced.(21) It takes less work for a polymer solution to cover a pigment particle if the energy at the interface is reduced. As surfactants work only on the surface properties of a liquid and not on the bulk properties, they are added in small amounts (usually <1 %). However, because the surfactants are an additive, the aging of the resins might be adversely affected. Surfactants can also be used with organic solvents. Here, the proper balance between volatility, viscosity and wetting would have to be determined. Future research should focus on commercially available surfactants, which have long been in use in the paint industry.(22)

Other methods for maintaining a matte appearance

Many conservators mentioned the use of matting agents, usually a resin solution containing silica, glass micro-spheres or other additives that reduce the gloss of a coating applied to the surface of the paint. However, correctly matching the original color and lightness of the paint in this manner could be quite difficult.

Thermosetting polymers polymerize or set *in situ*. They are not resolvable, but can have the desirable aspect of extensive three dimensional character resulting from cross-linking. If they react chemically with the substrate, a strong bond will be formed. As such, greater consolidative strength may be obtained

with a lesser amount of material in comparison to the previously mentioned resoluble, non-interactive thermoplastic resins which mechanically adhere particles together. These materials are not being proposed for the consolidation of painted ethnographic objects, but their evaluation for use is being proposed based upon the following desirable properties.

Weintraub and Greenland used an epoxy to consolidate a similar porous paint system, the deteriorating paint on early American stained glass.(23) Here, the application of thermoplastic resins had caused an unacceptable gloss and darkening of the painted surface. In contrast, a smaller amount of epoxy could be added with a much stronger bond and little change in appearance. The epoxy solution was sprayed on, and the surface subsequently matted with further solvent. The use of epoxies might be considered where a strong bond is necessary, where it is desirable that very little vehicle be added, or where a very thick paint layer is to be consolidated.

Agnew is exploring the use of a thermosetting polymer, a poly(urea), to consolidate adobe, which is a system similar to paint made from clay.(24) The starting material, a diisocyanate prepolymer, polymerizes *in situ* as a result of atmospheric moisture or moisture contained within the system. Very little shrinkage is observed as a film is not formed in the concentrations used. Moisture-curable resins also have the ability to form strong bonds in the presence of dirt(25) and might therefore be particularly suitable for the consolidation of ethnographic materials.

As with the thermoplastic resins, the application of solutions of thermosetting resins might also be improved in an atmosphere saturated with solvent vapor or by the use of surfactants. However, the aging characteristics of the materials have not been fully determined. In general, aliphatic diisocyanates should not have the yellowing problems often associated with epoxies.(26)

Conclusions

There are many criteria for the choice of a resin to consolidate painted ethnographic objects that must first be determined. Is the consolidation to last for one hundred years? In this case, there may have to be compromises in the acceptable limits of change in appearance because a large amount of a stable resin must be added.

In addition to the changes in appearance that result from the addition of a resin to a high PVC paint, localized surface concentrations or solvent interactions with components of the paint or wood may cause darkening, discoloration or increased gloss. Because application procedures can possibly be as important as, or more important than, individual resin properties in the effect on the appearance and on the strength of consolidation, the factors affecting these procedures should be considered as much as the physical properties of the resin.

Future research should focus on systematic comparisons of both materials and methods. When comparing consolidants, the amount of material added must be carefully determined and this has rarely been done in past evaluations. Until the stability of new materials has been fully established, experimentation should continue on improved methods of application of those resins known to possess exceptional stability, such as Acryloid B72 and PVAC. Exploration of the use of thermosetting resins may result in a wider choice for the conservator for particular consolidation problems when greater strength is desired.

Acknowledgements

We would like to gratefully acknowledge Sue Walston, of the Australian Museum, Sydney; Dr. Ruth Johnston-Feller and Dr. Robert Feller, Director Emeritus, of the Mellon Institute, Center for the Materials of the Artist and Conservator, Pittsburgh, PA; and Dr. Zeno Wicks, Professor Emeritus, of the North Dakota State University Coatings and Polymers Department, for their extensive comments and advice that added greatly to this manuscript; and, Dr. Frank Preusser, Dr. Neville Agnew, Michele Derrick, Marta de la Torre, Suzanne Deal Booth and Rima Nazarian, of the Getty Conservation Institute, for helpful suggestions while reviewing this manuscript.

Notes

1 R. L. Feller and N. Kunz, "The Effect of Pigment Volume Concentration on the Lightness and Darkness of Porous Paints," in AIC Preprints of the 9th Annual Meeting, Philadelphia.

Pennsylvania, ed. J. Johnson and M. Morales, (Washington, D. C.: American Institute for the Conservation of Historic and Artistic Works, 1981) 66-74.

2 The Consolidation of Painted Ethnographic Objects, a course presented by the Training Program, The Getty Conservation Institute, Marina del Rey, CA, June 11-29, 1990.

3 J. Holt, Tiwi Graveposts, (Melbourne: National Gallery of Victoria, 1988), 4.

4 E. P. Hatcher, Art as Culture: An Introduction to the Anthropology of Art (Lanham, MD: University Press of America, 1985), 74-76.

5 Feller and Kunz, "The Effect of Pigment Volume Concentration on the Lightness and Darkness of Porous Paints," 66-74.

6 Z. Wicks, Professor Emeritus, Polymer and Coatings Department, North Dakota State University, Fargo, ND, personal communication, January, 1990.

7 D. J. Lee, L. Bacon and V. Daniels, "Some Conservation Problems Encountered with Tumeric on Ethnographic Objects," Studies in Conservation, no. 30:4 (1985): 184-188.

8 J. Portell, "African Red Pigments," in Symposium 86: The Care and Preservation of Ethnological Materials, ed. R. Barclay (Ottawa: Canadian Conservation Institute, 1986) 119-129.

9 R. L. Feller, "Standards in the Evaluation of Thermoplastic Resins," in ICOM Committee for Conservation, 5th Triennial Meeting Preprints, Zagreb, (Paris: International Council of Museums, 1978) 1-11.

10 R. L. Feller and M. Wilt, Evaluation of Cellulose Ethers with Respect to Their Potential Long-Term Stability in Conservation Applications, (Marina del Rey, CA: The Getty Conservation Institute, in press) summary statement.

11 Feller and Wilt, Evaluation of Cellulose Ethers, summary statement.

12 R. L. Feller, Director Emeritus, Mellon Institute, Center for the Materials of the Artist and Conservator, Pittsburgh, PA, personal communication, November, 1989.

13 Feller and Kunz, "The Effect of Pigment Volume Concentration," 74.

14 S. Walston, D. Horton-James and S. Zounis, "Investigation into Methods and Materials for the Adhesion of Flaking Paint on Ethnographic Objects: A Progress Report," ICOM Committee for Conservation, 8th Triennial Meeting Preprints, Sydney, ed. K. Grimstad (Los Angeles: Getty Conservation Institute, 1987): 833-841.

15 E. Miller, N. Lee and D. Ellam, "Remounting and Conservation of Archaeological Wall Paintings," in Recent Advances in the Conservation and Analysis of Artifacts, ed. J. Black (London: Summer Schools Press, 1987) 289-296.

16 R. L. Feller, N. Stolow and E. H. Jones, Picture Varnishes and Their Solvents, (Washington, D.C.: National Gallery of Art, 1985), 137-145.

17 E. C. Welsh, "A Consolidation Treatment for Powdery Matte Paint," The AIC Preprints, 8th Annual Meeting, San Francisco, ed. M. Morales (Washington, D.C.: American Institute for the Conservation of Historic and Artistic Work, 1980) 141-150.

18 U. Schiessl, "Konservierungstechnische Beobachtungen zur Festigung Wassrig Gebundener, Kreidender Malschichten auf Holz," Zeitschrift für Kunsttechnologie und Konservierung, no. 2 (1989): 293-320.

19 Z. Wicks, personal communication.

20 E. F. Hansen, R. Lowinger and E. Sadoff, "Consolidation of Objects in a Solvent Vapor Saturated Atmosphere: A New Technique for Minimizing Changes in Appearance of Powdery, Matte Surfaces," in preparation, The Getty Conservation Institute, Marina del Rey, CA.

21 T. C. Patton, Paint Flow and Pigment Dispersion, (New York: John Wiley and Sons, 1979), 205-237.

22 R. Johnston-Feller, Mellon Institute, Center for the Materials of the Artist and Conservator, personal communication, October, 1989.

23 S. Weintraub and M. Greenland, "Field Application of Stained Glass Conservation Techniques," in Adhesives and Consolidants, IIC Preprints of the Contributions to the Paris Congress, ed. N. S. Bromelle, E. M. Pye, P. Smith and G. Thomson (London: International Institute for Conservation of Historic and Artistic Works, 1984) 199-201.

24 N. Agnew, Adobe Preservation: Report on a Three Month Research Effort at the GCI, (Los Angeles: The Getty Conservation Institute, 1986), 55-59.

25 A. H. Hughes, "Polyurethane Resins in Moisture Curable Surface Coatings," Journal of the Oil Chemists and Colourists Association, no. 1 (1986): 10-14.

26 Ibid, 10-14.

ABSTRACT

In order to assemble information on Dacca muslins and to identify lasting traces of its traditional technology, field research of materials and oral history, supplemented by literature surveys were undertaken. Jamdani, "the loom embroidered", is the finest product among all muslins and is the last remaining link in the long chain of Dacca muslins. Jamdani relates directly to the chikan, while the white muslin with embroidery is called nayan sukh. Jamdani, or figured muslin, evolved as an art fabric under the influence of Persian design. These muslins are considered masterpieces.

The present study includes research on manufacturing techniques, the implements used, the nature of the loom dyeing techniques, and the subsequent history and use of muslin and Jamdani. It also offers a comparative sketch of early and present methods of production.

KEYWORDS

MUSLIN, JAMDANI, WEAVER, RAW MATERIAL, SPINNER, PHOTEE KAPAS, CONSERVATION, SPINDLE, LOOM, DYEING.

MATERIAL CULTURE STUDIES OF DACCA MUSLIN

S.A.M. Monowar Jahan
Keeper
Conservation Laboratory
Bangladesh National Museum
Shahbag, Dhaka-1000
Bangladesh.

Introduction

Dacca muslin enjoyed a world-wide reputation as a highly artistic product and article of luxury which met the demands of kings and nobles. The word muslin is derived from Mosolins, a kind of cloth made of gold and silver from Mesopotamia, and has a quite different meaning from "Dacca muslin" (1). It is difficult to give a scientific definition of muslin. It is simply an open gauze-like veil fabric made with fine, specially spun and prepared yarns, and has a hazy appearance. Exquisite fineness, delicacy of texture and softness are the main characteristics of Dacca muslin. The infinite patience and the delicate treatment of the fabric by the female spinners are the real sources of its excellence.

Plain and embroidered muslins are used for making finer quality garments for men and women. Koorta (a loose shirt), turban (headress), chupkan (long gowns for men), and jamah (dress gown) were all suitable for hot weather; scarves, neckerchiefs, and dresses were made for women. Jamdanis are mainly used as sarees, the chief article of female attire. The use of Jamdani fabric has diversified and is currently also widely used for making dresses like koorta, kameez and salwar.

Old textiles are rare, and very few museums have a truly representative collection of muslin and Jamdani. In Europe, the Victoria and Albert Museum has a good collection of muslins and Jamdanis; the museums of India and Bangladesh also have valuable collections of both Jamdanis and muslins. A piece of muslin in the Bangladesh National Museum measures 910 X 87.5 cm and weighs 84.2 grams. The piece is very soft and transparent. This museum also has fine collection of Jamdani.

The fine muslins are no longer made. The lack of patronage by the Mughal imperial and vice-regal courts, and the imposition of tariffs by British rulers influenced the decline of the old race of katanis (female spinners) and skilled weavers, which in turn decreased muslin production.

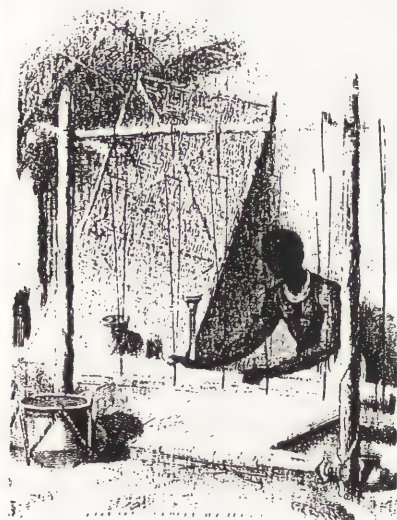
Raw materials

The cotton fibre comes from the fruit of the cotton plant which grows in the tropical regions. The vernacular name of the finest Dacca cotton is photee kapas. Most early writers describe muslin cotton as a short stapled annual plant. One of its special characteristics is that the wool adheres quite tenaciously to the seed. Its fibre is more fine and silky than that of any other variety of cotton (2).

Dacca cotton is suitable for spinning the most delicate hand-spun yarn, although it has a shorter staple. Due to the greater elasticity of the fibres of cotton it is capable of receiving more twist than other types of cotton, and thread made from it does not swell after bleaching.

Raw cotton consists principally of cotton seed oil, pectic acid, colouring matter, albumin and wax. The wax acts as a protective coating to the fibre, making it water repellent. Bleached cotton is almost pure cellulose.

Muga silk: The 'Muga-moth' is a species that is somewhat domesticated in this subcontinent. The muga silk is superior to the tassar with regard to gloss and other qualities. Generally, it is employed for the manufacture of mixed fabrics and some kinds of embroidery (3).



A Tanti weaving muslin
Sketched by C.D'Oyly between
1814-1827

Metallic yarn: Manufacturing fine gold and silver thread for the weavers and embroiderers became a speciality of Dacca. Metal threads are incorporated into muslin and Jamdani. Any of the ductile metals, such as gold, silver, copper, or even the cheaper alloys can be drawn out into fine filaments.

Modern metallic yarns are generally made of coloured aluminium ribbons sandwiched between two layers of transparent plastic. These are light weight, bright, nontarnishing, and relatively inexpensive yarns. The yarn can withstand bleaching and is resistant to insect and moth attack, mildew, and rot. Metal threads are made by wrapping a metal ribbon around a core of cotton yarn.

Charcoal powder, lamp black or soot are used in the processing and preparation of yarns. Rice water, rice paste, and lemon-juice are also used in this process (4).

Spinning tools and appliances: The process of spinning the finest yarns for the production of muslin was different in some ways from ordinary handspun thread. The seeds were carded with the jawbone of the wallago atta fish goal. Utmost care was taken to detach the fibres from the seeds; the implement used was a dalan cathee, or simply an iron rod rolled upon a flat wooden board. The thread was spun on a tukua, or delicate spindle (5). The spinner draws out the filaments from the roll of cotton and twists them into yarn upon the spindle. It appears from the authors investigation that the superior fineness of Dacca yarn depends chiefly on the smaller number of filaments. The time and skill required in spinning very fine yarn was very costly. As there is currently no demand or market for muslin, the yarn of the Dacca standard could not be economically produced, and ultimately the art of spinning passed into history. Fortunately, Jamdani, the majestic variety of muslin, still survives. The skill of Jamdani weaving was not totally lost but was adapted to changing times.

Construction of Loom

The weavers looms have remained unchanged over the centuries. The actual processes of weaving the Dacca muslins and the appliances used are identical to those used for Jamdani. Very simple implements are required for the construction of loom.

The total number of the implements used in converting the raw materials into thread, and weaving this thread into exquisite Jamdani or muslin is 126. They are principally composed of bamboo and reed. Noapara and Siddhirganj are the homes of master weavers; these two existing Jamdani villages are situated on the outskirts of Dacca, along the river Sitalakhaya.

The important implements used in the construction of a loom are described below.

kandur is a simple needle made of bamboo, wood or bone, which is used to take in and out of a fixed number of warp threads. It is about 8 cms long.

Shana is the reed made of bamboo, which is 130 x 4 cm. The finest reed used in the Dacca loom contains 2800 dents in a 130 cm space. Two reeds are used in the loom.

Narad is the yarn beam, generally made of wood. Two beams are used, one is called a "cloth beam", or "breast roll", and the other is called a "yarn beam".

Maku is the shuttle made of wood. It is 33 cm long, and mounted between spear-shaped pieces of iron. This holds the filling, or weft yarn. Jamdani weavers use a "pit-type throw shuttle".

Boya is similar to the reed but its dents are made of yarn. Its dimensions are identical to those of the shana.

Muti kamani is the temple for stretching the cloth during the process of weaving, and is formed of two rods which are connected with rope or cord, and fastened at their outer ends with two brass hooks.



Kandur



Maku

Muti kata is the brass pin or hook.

ubi are four bamboo posts firmly fixed in the ground; each post is 2 meters in length.

Chowchala are two bamboo poles fixed above as side pieces which support the transverse rods.

Bish karamer khuta is the shoulder post which supports both ends of the breast roll.

Talpati are treadles made of bamboo pieces, and are contained in a 0.90 x 0.65 x 0.46 meters pit dug in the ground.

Duktis are two wooden pieces which are used as a frame for mounting each set of reeds.

Fundi are small reeds used for weaving borders.

Jutadari are jute ropes used for tying treadles.

Babri are two bamboo bars tied to the four bamboo posts.

Daris are the approximately one hundred jute ropes of different lengths which are required for the construction of the loom.

Muni is a bamboo post, and khilis are wooden pegs.



The loom and the jamdani weavers.

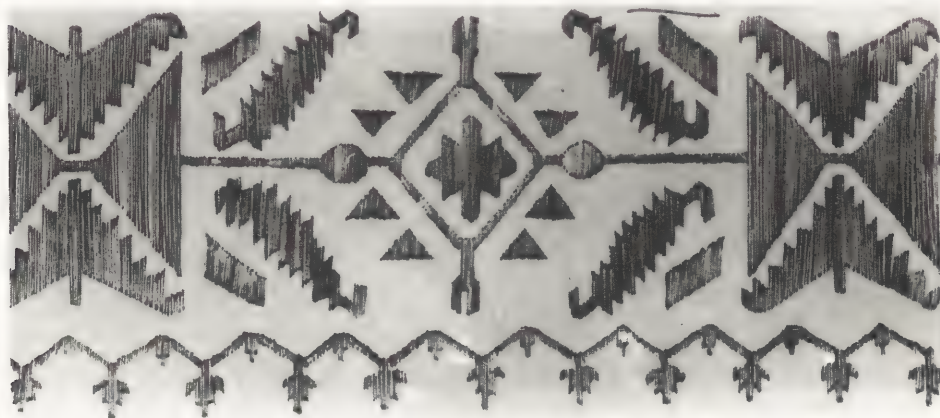
Weaving

The production of Dacca muslin was done by small master weavers who owned from two to eight looms. Muslins were woven by tantis (Hindu weavers), and Jamdanis by julahas (Muslim weavers); the latter cloth continues to be the exclusive domain of muslim weavers to the present time (6). Once the warp threads were arranged, two weavers sit at each loom; the main weaver is karigar and nikari is the apprentice. The weavers keep no charts or records, and the designs have been handed down over many generations. Each weaver stores these designs in his memory to reproduce by his magical touch at the loom.

Using a small finely-pointed bamboo or tamarind wooden needle, they draw as many threads of the warp as may be equal to the width of the figure which is to be formed. Each length of this thread merges with the weft, and additional lengths are added until the motif is completed. When all the threads have been brought between the warp, they are drawn close together by a stroke of the lay.

The shuttle is then passed by one of the weavers through the shed, and the weft is driven home and returned by the other weaver. Thus in rhythmic fashion the weavers embellish cloth with delightful variations.

At present, reeds used for weaving Jamdani contain about 2000 dents in a 130 cm space. Two hundred and thirty three grams of warp thread are required for four pieces of sarees; each measures 500 x 110 cm. Silk yarn is used for the warp threads; these are not visible, and only the weft thread design floats on the surface texture of the fabric. Jamdani designs are composed of unique geometric representations of fruits, flowers, leaves and creepers skillfully devised to adapt to the weave of the material. Various angular, circular and semicircular designs are formed as wefts of coloured threads cross the warp.



Geometric design on jamdani

Rice starch is used as a stiffening agent for Jamdani. The starch grains are very small and penetrate the fabric thoroughly. The weaver keeps ground boiled rice at the side of the loom, and during the process of weaving, they smoothly apply starch on the cloth beam with their fingers.

Dyeing

Both chemical and vegetable dyes are used in dyeing yarns for Jamdani. Vegetable dyes are very popular because of their attractive soothing colours; they have the added advantage of having non-pollutant and non-allergenic characteristics. With the re-introduction of natural dyes, a wide new range of unusual and subtle colours has been developed from the following natural sources:

Leaf of indigo
Indigofera tinctoria

Scale leaf of onion
Allium cepa

Sap of catechu
Accacia catechu

Fruits of myrabolan
Terminalia chebula

Bark of minor
Heritiera

Swadust of jackfruit
Artocarpus integrifolia

Nut of betel-nut
Areca catechu

Fruits of mangosteen
Diospyros peregrina

Stem of cardifolia
Rubia tinctorium

Rind of pomegranate
Punica granatum

Leaves of basil
Ocimum sanctum

Leaves of henna
Lawsonia inermis

These materials have been used to produce 14 basic colors blue, red, green, yellow, orange etc. Combination of these produce additional varieties of shades (7).

Before dyeing, the hank yarn is subjected to mordanting. The method of dye extraction and dyeing is the same for most dyes, except catechu and indigo, which have completely different procedures. The raw materials are boiled in equal quantities of water for 30 minutes; then the dye can be extracted by straining

the solution through a fine cloth.

After removing the yarn from the mordant solution, excess water is squeezed out. The yarn is then put into dye solution and boiled for 30 minutes; any excess colour is then washed in plenty of plain water. It is better to use soft water for dyeing. The water of river, lakes and well are therefore the most desirable, and are also good for washing.

Washing and preserving Jamdani is very difficult. The special system of washing and the later replacement of the thread in its proper position is called katakara. Jamdani is washed in cold water with soap and washing soda, and then starched with arraroot and dried. Again it is wet and rolled in a roller and the other end is fixed to another roller in a stretched position with clops. Then a brush made of metallic pins is drawn along the surface of the displaced threads to bring them into their proper places.

Conclusion

Muslins are no longer made but the Jamdani crafts which still survive are a vital part of the cultural heritage of Bangladesh. Research and documentation of fabrics in museums and private collections may yield a fair collection of classical designs which can be reproduced with precision and sensitivity by the master weavers.

NOTES

1. J.C.Sinha, "The Dacca Muslin Industry" in Modern Review (Calcutta: April, 1925), 400.
2. Ibid., 402.
3. S.Dantiyagi, Fundamentals of Textiles and their care (New Delhi: Orient Longman, 1974), 77.
4. Forbes J.Watson, The Textile manufactures and the costume of the people of India (London: printed for the India office, 1860), 66.
5. James Taylor, Sketch of the topography and statistics of Dacca (Calcutta: Government publication, the Huttman Military orphan press, 1840), 166-167.
6. Sayyada R.Ghuznavi, "Jamdani" in Woven Air (London: White Chapel Art Gallery, 1988), 52.
7. Sayyada R.Ghuznavi, Rangeen: Natural Dyes of Bangladesh (Dhaka: Vegetable Dye Research and Development Society, 1987), 24.

RESUME

Restaurateur, Consultante
ACCT et UNESCO, formatrice
de techniciens dans des mu-
sées ou sur des chantiers
archéologiques, confrontée
-sur le terrain- aux pro-
blèmes de différents pays,
j'ai recherché, avec l'aide
de Stagiaires ou d'Anciens,
des moyens traditionnels de
PRESERVATION des objets eth-
nographiques.

Dans ma communication de
LA HAYE (30 Août 1989) pen-
dant la XVème Conférence
Générale de l'I.C.O.M. ,
"PROTECTION ET CONSERVATION
DES OBJETS ETHNOGRAPHIQUES
DANS LES PAYS AFRICAINS",
je présentais beaucoup d'ob-
jets, le plus ancien étant
un "BALAFON" du XIIIème
siècle, préservé par les
"ANCIENS" au cours des siè-
cles grâce aux moyens tradi-
tionnels . Des chercheurs
m'ont demandé d'expliquer
ces procédés archaïques mais
efficaces .

J'inventorie donc quelques
moyens de conserver des ob-
jets Africains, même si on
ne possède aucun produit ou
infrastructure modernes et
j'engage vivement le person-
nel des Musées à utiliser
ces procédés afin de sauver
les oeuvres dont ils sont
responsables .

MOTS-CLES

Conservation, objets ethno-
graphiques, diverses régions
Africaines, méthodes tradi-
tionnelles .

METHODES TRADITIONNELLES ET LOCALES DE CONSERVATION DES OBJETS
ETHNOGRAPHIQUES DANS DIVERSES REGIONS AFRICAINES .

Colette Jourdain
Conservateur-Restaurateur
Service Archéologique, Musée d'Aquitaine
Mairie de BORDEAUX, 33000, FRANCE

1. Introduction

Si certains " Conservateurs-Restaurateurs " peuvent compter sur
les Sciences les plus modernes pour étudier, conserver et restau-
rer les objets, et s'il est indispensable d'avoir des Laboratoi-
res de Recherche travaillant pour l'avenir, nous constatons que
les problèmes de conservation des objets ethnographiques sont les
mêmes partout dans le monde et qu'il est urgent de rechercher des
solutions rapides afin d'éviter les problèmes de détérioration,
certains identiques de par leur zone géographique, par exemple,
dans les zones tropicales situées sur des continents différents.
Cette situation que les Consultants ACCT ou UNESCO connaissent
bien a une telle ampleur qu'il ne faut surtout pas négliger ces
objets car ils sont en voie de disparition (1).

Conditions climatiques, manque de spécialistes, petit budget con-
sacré la plupart du temps au Département Culturel d'un pays, dif-
ficultés pour se procurer sur place certains produits, frais de
transport et de douane, délais de livraison, sont les principales
difficultés rencontrées .

Aussi faut-il se servir le plus possible de ce que l'on peut
trouver sur place et pratiquer les procédés de préservation des
"ANCIENS", lorsque l'on peut les obtenir et les inventorier .

2. Afrique Septentrionale .

2.1. Dans l'ancien ROYAUME HAFÛIDE DE TUNIS (actuelle TUNISIE),
le principal handicap des objets situés près de la mer est l'
humidité . La méthode traditionnelle de protection des bois
peints et sculptés consiste à les enduire d'huile d'olive, de
même que les peintures sur bois et sur verre . Tissages, tapis,
tissus et vêtements étaient conservés dans des coffres herméti-
ques en bois et en métal après un séchage prolongé au soleil,
s'ils avaient été mouillés .

En bordure du Bassin Méditerranéen, pour restaurer des poteries
comportant des "manques", notamment amphores et vases à hauts
cols, une méthode traditionnelle consiste à remplir l'objet de
sable mouillé afin qu'il durcisse . A l'emplacement de la partie
manquante, on applique au préalable une feuille de papier pour
empêcher le sable de sortir . Lorsqu'il est dur, on enlève le
papier, puis on pose le plâtre que l'on modèle afin que l'objet
retrouve sa forme . Il ne reste plus qu'à laisser sécher le sable
au soleil . Il s'écoulera seul après évaporation de l'eau . Mais
les terres cuites se conservent très bien partout.

2.2. Arbres méditerranéens . Il y a peu de bois, mais on trouve:
"palmier-dattier", arbres fruitiers , "olivier", servant tous
pour la restauration . On importe un bois brun pour la menuiserie
et un "bois blintz" pour les sculptures .
La liste des arbres selon les pays étudiés n'est pas limitative.
Ce sont ceux servant pour la sculpture, bois de menuiserie pour
les habitations, ou servant traditionnellement pour la préserva-
tion des objets sacrés . Chaque arbre a sa vertu magique et sa
propre utilité pour la vie villageoise .

3. Afrique Occidentale Soudanaise .

3.1. En Afrique subsaharienne, dans les anciens ROYAUME BAMBARA
DE SEGOU (actuel MALI), EMPIRE MOSSI (2) (ex HAUTE-VOLTA, actuel
BURKINA FASO), ETAT HAOUSSA et EMPIRE SONRHAY (actuel NIGER), les
problèmes habituels aux pays d'AFRIQUE se retrouvent avec, en
plus, ceux des Régions Sahéliennes, chaleur et sécheresse . Les
écarts de température étant très nocifs aux objets ethnographi-
ques, un des problèmes majeurs est la conservation du bois ainsi
que celle des costumes régionaux anciens lorsqu'ils ne sont pas
protégés dans les cases villageoises . Avant d'utiliser du bois
neuf, on le frotte avec de l'huile de palme afin d'éviter son
fendillement .

La plupart des terres sont ferrugineuses et les poteries permet-
tent d'entreposer les produits servant à la protection des métaux
et des bois pour lesquels on utilise partout les mêmes procédés
de conservation traditionnelle . On enduit l'objet de produits
oléagineux d'origine animale et végétale : beurre de lait de
vache, beurre provenant des noyaux contenant l'amande écrasée du
"karité" poussant dans la savane soudanaise . Ensuite, exposition
prolongée au soleil, provoquant néanmoins certains méfaits sur
les tissus . On procède également par fumigation .

Les calebasses, fruits coupés en deux, vidés et séchés du "lagenaria-vulgaris", ou "calebassier", sont parmi les récipients les plus anciennement fabriqués par l'homme. Remplissant un grand nombre de fonctions domestiques, d'emmagasiner, de transport, et extrêmement appréciées pour leur poids léger, leurs formes et tailles variées, elles servent à entreposer les produits de protection. En guise d'éponges, les boules d'herbes ou de fibres végétales, économiques, très efficaces et les petits balais ou les brosses, poignées de graminées locales liées ensemble, sont faciles à renouveler. La bouse des bovidés mélangée à la paille, façonnée en galettes séchées au soleil, peut servir de combustible, à défaut de bois, si l'on veut chauffer l'huile protectrice. Une boulette, argile et cendre mélangées, remplace le savon pour le nettoyage des objets.

3.2. Arbres Sahéliens. "Siyan" en savane malienne, "kapokier", bois léger, "baobab", "karité", "fromager", "caillcédrat", "manguier", "rônier", "palmier-doum" représentatif du NIGER, "nééré" ("nété" en MOSSI), donnant des graines formant la pâte du condiment le "soumbala" (appelé "kologo" en MOSSI, "zoolgo" en langue MORE, ou "soumbara" en DIOULA). Après le séchage, les graines sont bouillies puis pilées. Ce procédé existe aussi au nord du BENIN mais pas au NIGER. Le "tamarinier" donne un suc servant pour la restauration. Le "gao", rencontré partout en brousse, a la particularité de conserver ses feuilles en saison sèche.

4. Bordure Atlantique de l'Afrique Occidentale.

4.1. Au ROYAUME D'ABOMEY (ancien DAHOMEY, actuel BENIN), les objets sont particulièrement en danger en région tropicale. Les conditions climatiques, chaleur et humidité avec leur accompagnement d'insectes, de parasites, de bactéries et de moisissures, fortes chaleurs et sécheresse, brusques variations de température pouvant exister en moins de vingt quatre heures, néfastes aux bois, forte humidité de certains climats provoquant l'instabilité des métaux, sont mauvaises mais ont toujours été vaincues par les ANCIENS. La méthode locale de traitement des objets consiste à les enduire de beurre de karité ou d'huile de palme, le badigeonnage s'effectuant à l'aide de queues de cheval. On procède aussi à des fumigations, à des séchages ou des expositions prolongées au soleil qui joue un rôle très important en AFRIQUE. Les textiles, costumes et tapis sont fabriqués avec des fils de différentes matières animales ou végétales, la meilleure conservation consistant à les garder pliés dans des paniers à l'intérieur des cases.

4.2. Dans l'ancien EMPIRE DU FOUTA-DJALLON (actuelle GUINEE), en forêt, une méthode traditionnelle consiste à mettre de la poudre de piment à l'intérieur des vases rituels en bois. Le piment a été, au préalable, séché longuement au soleil avant d'être pilé. On emploie également la bouse de vache mélangée à la terre. On enduit aussi le bois de kaolin. En savane, les branches du "siyan" se taillant très finement servent pour les réparations délicates. Lorsqu'un objet en bois blanc "bois de fromager", est attaqué par les insectes, on le badigeonne à l'huile avec une queue de vache ou avec des plumes d'oiseaux, puis on l'expose au soleil afin que le bois ne change pas de couleur en séchant. On extrait des solutions d'écorces d'arbres : "sugbala" donnant un rouge violacé, "babgé", "sisabofida", "siby", "lingui", "kolokolo" (noms en langue MANINKA). Ces arbres sont choisis par les Anciens qui connaissent les propriétés de chacun pour protéger les objets. On laisse déposer la décoction, on la passe sur l'objet à protéger et on l'expose au soleil. On frotte les objets en bois dur avec la sève extraite d'un "caillcédrat", puis on l'expose au soleil. La colle en coulant sous l'effet de la chaleur pénètre dans le bois. On utilise des badigeonnages à l'huile de palme ou la fumigation dans les cases où un feu est entretenu en permanence. Un instrument de musique, un "BALAFON" du XIII^e siècle, a bénéficié de conditions particulières de préservation (3). Il se trouvait dans des cases où la fumigation naturelle le conservait. Les conditions climatiques et atmosphériques étant les mêmes au cours des siècles, il était encore en 1984 en parfait état de conservation à NIAGASSOLA, dans la région de SIGUIRI. La plupart des objets étant fabriquée en matières organiques ou végétales, dans les campagnes et la plupart des petits musées, seuls les procédés de conservation traditionnelle peuvent être utilisés.

4.3. Arbres de la zone côtière Occidentale. La forêt est la même au BENIN, en COTE D'IVOIRE et en GUINEE. Certains arbres sont couramment utilisés pour la restauration ou la construction : "teck", "acajou", "ébène" pour la sculpture, "acacia", "arbres fruitiers" pour leurs branches, leurs feuilles, leurs jus. Au FOUTA-DJALLON, le "linké", grand arbre très résistant de cou-

leur rouge, sert pour les madriers, la menuiserie et pour sa poudre. D'autres arbres sont représentés : "kolatier", "caïlcédrat", "palmier à huile", "cocotier", "caféier", "sembagbali". Dans la Savane Guinéenne : "siyan", une variété d'"iroko", sur la Basse Côte : "acajou" et en MANGROV littorale beaucoup d'arbres fruitiers. En régions montagneuses, le "pourgere" donne des haies vives que l'on taille facilement.

5. Afrique Centrale .

5.1. Dans l'ex ROYAUME DE FOUMBAM (à l'ouest de l'actuel CAMEROUN), une des obligations ancestrales est le respect de la personnalité de l'objet. Certains objets de culte sont recouverts de noir de fumée, tels les masques-heaumes des BA'NGWA. Ils sont gardés dans les poutres du toit, près de l'endroit où se trouve le foyer central servant à la cuisson des aliments, surmonté d'un fumoir-séchoir. Progressivement le noir de fumée se dépose. En aucun cas il ne faut l'enlever car cela protège l'objet qui doit, en outre, rester dans l'état où il se trouvait lorsqu'il servait régulièrement. Cette coutume locale rejoint la préoccupation des ethnographes : présenter l'objet tel qu'il était autrefois. Pour nettoyer et rénover les cuirs, un procédé très simple, peu coûteux et facile à réaliser partout où l'on trouve des bananes, petites vertes ou grosses bananes "plantains", consiste à peler ces fruits et à frotter l'objet avec l'intérieur de la peau en insistant sur les parties abîmées. On laisse sécher cette pâte, puis on fait briller le cuir avec un morceau de pagne. La pulpe nourrit le cuir en le faisant briller et en le rénovant, particulièrement s'il est de teinte beige ou marron, la banane ayant tendance à foncer le cuir blanc. On utilise l'"huile de coprah", d'"arachide" ou de "pied de boeuf" pour les pièces très sèches.

5.2. ROYAUME DU KONGO .

5.2.1. PAYS DES BANTOUS, puis DES FANGS (actuel GABON), au cœur de l'Afrique équatoriale, d'épaisses frondaisons bordent le fleuve OGOOUE. Les statuette-fétiches en bois et leurs "ingrédients", les figurines BAKOTA (4) recouvertes de laiton, présentent des difficultés de conservation. Le mot "fétiche" d'origine "moundélé" ("le blanc" au CONGO), fut employé par les Européens lorsqu'ils sont arrivés en AFRIQUE. En réalité, ce sont des statuettes rituelles, participant au Culte des Ancêtres. L'ethnie KOTA (4) provient de la région du NIARI ou de la LEKUMU au CONGO et s'étend jusqu'au GABON. La principale difficulté de conservation de ces statuettes sacrées provient du fait qu'elles ont des réceptacles situés sur le ventre, dans lesquels se trouvent des produits ayant pour but, lorsqu'elles ont été sculptées de rendre les statues "actives" : ingrédients humains, glu, terre ... Parfois un morceau de miroir ferme le réceptacle. Il ne faut pas y toucher et ne pas chercher à l'ouvrir, pour ne pas l'endommager et surtout "par respect". Pour leur teinture, les sciures du "paduk", bois rouge et la sciure jaune de l'"iboga", mélangées à l'huile de palme sont très utilisées. Dans les villages, une protection simple et efficace consiste à les enduire d'huile de palme chauffée ou d'huile de "palmiste". On y trempe les objets qui sont ensuite séchés au soleil. On pratique aussi la fumigation à l'intérieur des cases, "la fumée protectrice". La conservation des peaux de bêtes en zone tropicale est assez difficile. Certaines poudres provenant d'un arbre à piments de la forêt donnent une protection provisoire.

5.2.2. Cuvette Congolaise, Pays TEKE, Région des Pools (actuel CONGO) .

Au ROYAUME DE LOANGO, établi sur la rive droite du fleuve CONGO, le climat équatorial chaud et humide, la forêt vierge d'une partie du pays et les vallées marécageuses des grands fleuves donnent une richesse végétale renfermant d'innombrables plantes utilisées depuis les temps les plus reculés par les Anciens. La base de la culture des ethnies si différentes peuplant ces régions étant le Culte des Ancêtres, les statuettes rituelles en bois sont préservées par les Anciens comme en pays FANG. Parfois les sculptures sont fendues. Cela vient du fait que le bois, se taillant plus facilement à l'herminette ou au couteau juste après la coupe de l'arbre, "vert" ou "à l'état frais", quelques fêlures apparaissent en cours de séchage. Colle à froid provenant de l'"hévéa" et sciure sont glissées dans les endroits lézardés. Les fibres provenant du tronc du "bananier" et ses lamelles servent à consolider les objets en bois. Les instruments de musique sont traités par un remplissage à froid de sciure de "bois de cam", plus une colle végétale. Après un séchage prolongé au soleil la plupart des parasites sont tués. Les termites représentent un très grave problème sur ce continent. Les nervures de la palme du "piki" (en KONGO-LARI), palmier sauvage produisant le raphia sont des fibres souples, douces et solides

servant notamment pour la confection et la réparation des fils de cithare .

Au ROYAUME TEKE (5) ou TYO, sur la rive droite du STANLEY POOL, "hévéa", "bois de palétuvier" très léger servant à de nombreux usages, principalement aux masques KIDUMU (groupe ethnique TEKE de la frontière CONGO-GABON), "ananas" dont on extrait le fil de son feuillage, "piki", servent pour la restauration des objets domestiques ou rituels .

Les pagnes BATEKE (5) en fibres végétales sont parmi les plus beaux . Leur tissu de raphia teinté est souple, d'une grande finesse , d'une grande variété de tonalités provenant du suc de plantes et protégés par imprégnation de sciure de bois de "cam" et fumigation .

Les pots-"canaris" de la REGION DU POOL, sont très fragiles et conservés sans être mouillés extérieurement, avec beaucoup de soins car ils sont en voie de disparition . Ces pots pétris d'une argile spéciale appelée "lubumba" chez les KONGO-LARI, ont un décor fait avec les feuilles d'un arbuste "n'kolokoto", appliquées sur la terre glaise avant la cuisson pour laquelle on utilise le bois de ce même arbuste appelé également "kinzu" en LARI . Elles forment des dessins très décoratifs lorsqu'on les enlève .

Le kaolin est utilisé pour blanchir les objets, masques et tombes qui sont badigeonnées régulièrement par respect familial .

Le polissage de l'ivoire se fait avec une peau de bufle sur laquelle on pose un peu d'abrasif tendre, telle la poudre d'os animaliers tamisée . Mélangée à l'eau, elle donne une pâte molle .

La polychromie des bois de type PUNU, groupe ethnique limitrophe CONGO-GABON, blanc, rouge et noir, doit être traitée avec beaucoup de précautions afin de ne pas altérer ou supprimer les couleurs qui proviennent de terres de tonalités différentes . On les restaure avec ces mêmes poudres .

5.2.3. Rive gauche du CONGO . Cette partie du ROYAUME DU KONGO (ancien CONGO belge, actuel ZAIRE) ressemble dans sa partie occidentale à la rive droite du fleuve pour les méthodes traditionnelles de conservation . Dans les villages, les objets culturels en bois sont protégés par l'écorce pilée du "sokosoko", mélangée à l'huile de palme chauffée, puis injectée dans les trous d'insectes, huile extraite des noix grillées, suivie d'une exposition prolongée au soleil . C'est ainsi qu'un tambour KUBA (6) du XVII^{ème} siècle provenant du KASAI occidental a été conservé jusqu'à nous (7), les BAKUBA (6) formant un groupe ethnique du nord du pays . L'huile peut être mélangée à la poudre du "toukoula" . Le problème important pour les Anciens était de protéger le célèbre "velours" du KASAI, tissu en fibre végétales brodées, très épais, servant à enterrer les morts au ROYAUME KUBA . Leurs corps en étaient entourés . Tissu fragile, les insectes se cachaient dans son épaisseur . La sciure du "kamba" imprégnant ces velours sert de protection pour leurs fibres, de même que la fumigation dans les cases .

5.3. Arbres d'Afrique Centrale .

La forêt vierge bordant l'OGOOUE possède une grande variété d'arbres donnant des bois de couleurs différentes : "okoumé", bois tendre, rouge, "paduk", "ébène", bois noir très dur, "limba", dur, très résistant, "parasolier" appelé "arbre du voyageur", "acacia", "atangatie", "acajou" ou "ombéga", "ozipo", "sipo", "bilinga", "iboga", bois jaune, "bambou", "sagoutier" (surtout dans les villages équatoriaux du sud camerounais) .

Le long de l'OUBANGUI, en forêt vierge : "palmier-bambou", "rotin", "pandanus", "papyrus", "ébénier", "acajou jaune", "okoumé", "bois de santal", "kolatier", "kapokier", "copalier", "atanga", "ireh" (dans le bassin de la SANGA) .

Sur la rive droite du CONGO, les arbres sont nombreux . Outre ceux déjà cités : "palmier-raphia", "palmier à huile", "arbres fruitiers", "bananier", "manguier", "ébène", "fromager", "baobab", "parasolier", "combo-combo", "lingué" fournissant du jute .

Sur les plateaux BATEKE : "hévéa", "palétuvier", "ananas", "piki" .

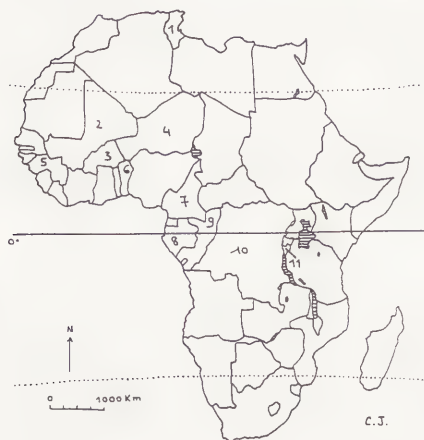
Sur la rive gauche du fleuve, les arbres : "flamboyant", "cocotier", "ébène", "ifak", "baobab", "kamba", "palmiers", "sokosoko", "toukoula", donnent une diversité de couleurs : blanc, rouge, noir, jaune, ocre, marron

Selon les pays, les arbres portent des noms différents : le "bois de cam", parfois appelé "iroko" au CONGO, devient "kamba" au ZAIRE, "iroko" au BENIN et en GUINEE . "Paduk" au GABON, ce bois devient au ZAIRE, venant de N'GOLA au KASAI occidental "toukoula", ou "loukoula" . On dit "ébénier" ou "ébène" .

6. Afrique Orientale .

6.1. Au ROYAUME DU BOUROUNDI (actuel BURUNDI), dans la Région des grands lacs, l'humidité constante et la chaleur règnent presque

CARTE DES PRINCIPAUX PAYS
AFRICAINS CITES DANS LE TEXTE



Noms actuels de pays formant
jadis des Royaumes dont les
ethnies ont parfois été
divisées au cours des siècles.

1. TUNISIE
2. MALI
3. BURKINA FASO
4. NIGER
5. GUINEE
6. BENIN
7. CAMEROUN
8. GABON
9. CONGO
10. ZAIRE
11. BURUNDI

toute l'année . La conservation traditionnelle dans les villages consiste à remplir les calebasses avec du beurre tiré de la séparation du lait de vache et du petit lait . On en frotte les objets afin de les protéger . On utilise également l'huile de palme pour protéger le bois, réparé grâce au kaolin, argile blanche très pure ajouté à la terre glaise . La fibre des "flamboyants" est utile pour réparer les objets domestiques, culturels ou instrumentaux . Une excellente protection est la fumigation dans les cases .

6.2. Arbres d'Afrique Orientale . On utilise une variété de bois blanc, l'"*éritrina abyssinica*" pour les mortiers et les sculptures blanches, puis : "palmiers à huile", "eucalyptus", "flamboyant" décoratif, "grévillia" pour sculpter des sièges, "cédrelat", bois rouge pour la menuiserie et la conservation, "calebassier" .

7. Conclusion .

La PRESERVATION est la meilleure mesure de conservation pour un musée sans moyens importants .

"RASSEMBLER", "CONSERVER", c'est-à-dire "SAUVER" les oeuvres d'art, voilà le plus urgent, avant de penser à la présentation au public et pour revaloriser les patrimoines culturels . Les objets culturels des Anciens, les collections gardées par le peuple, parfois cachées dans des cases de la forêt équatoriale où nul "moundélé" (8) ou membre d'une autre ethnie ne peut pénétrer, prouvent que les Africains conservent un profond respect pour les objets du passé .

Mais "SAVOIR ET SAGESSE DISPARAISSENT AVEC LES ANCIENS" . C'est pourquoi il faut s'attacher à conserver cette tradition orale, qui permettra de connaître dans le futur, des modes de vie, des traditions et des coutumes qui auront totalement disparus .

Soleil, huile de palme, d'olive, beurre de karité, poudre de piment, fumigation, ces mots peuvent sembler dérisoires et archaïques aux côtés de "Commissariat à l'Energie Atomique", "Centre d'Etudes Nucléaires", "Centre d'Etudes Spatiales", mais n'oublions pas qu'il n'y a pas de beaux objets de collection et d'autres, fragmentés ou usuels, longtemps ignorés ou méprisés . Chaque objet a son importance pour la connaissance du passé et si on ne peut le sauver que par des méthodes traditionnelles de conservation et des produits locaux, il faut le faire .

A NOK (actuel NIGERIA), des poteries remontent à 2000 ans, comme l'a prouvée la méthode scientifique de la thermoluminescence .

L'ARTISANAT PEUT PRODUIRE DES OEUVRES QUI SONT DE VERITABLES OEUVRES D'ART, NE L'OUBLIONS PAS ET SONGEONS TOUJOURS QU'UN AFRICAIN NE FAIT PAS DE DISTINCTION ENTRE L'ART ET L'ARTISANAT, CE QU'IL UTILISE, CE QU'IL PORTE ET CE QUI L'ENTOURE . ARTISTE DE NAISSANCE, SON NIVEAU D'ART EST, CERTES, ELEVE, MAIS CE N'EST POUR LUI QUE LA TRADITION PERPETUEE .

8. Notes .

1. Colette JOURDAIN . "Nécessité de sauver les Objets Ethnographiques Africains en voie de disparition" (Intervention faite à la XIV^{ème} Conférence Générale de l'ICOM, table ronde Comité International Conservation, BUENOS-AIRES, ARGENTINE, novembre, 1986) .

2. MOSSI, singulier de MOSSE , EMPIRE DU MOOGHO (BURKINA FASO).

3. 7. Colette JOURDAIN, "Protection et conservation des Objets Ethnographiques dans les pays Africains" (Communication faite à la XV^{ème} Conférence Générale de l'ICOM, Comité International Ethnographie, LA HAYE, PAYS-BAS, Août, 1989), 12 .

4. BA sert de pluriel en AFRIQUE CENTRALE . KOTA , BAKOTA .

5. TEKE , BATEKE .

6. KUBA , BAKUBA .

8. MOUNDELE, pluriel MINDELE .

9. Références .

Je remercie infiniment mon frère Congolais, tous les amis et Stagiaires Africains ACCT ou UNESCO, techniciens, avec lesquels j'ai travaillé, en AFRIQUE ou en FRANCE, ainsi que les ANCIENS qui m'ont tous transmis, par la voie orale des connaissances et des pratiques ancestrales que j'ai expérimentées et utilisées chaque fois que les moyens modernes me faisaient défaut . Leur confiance m'a aidée à mieux connaître et à mieux comprendre l'AFRIQUE .

Working Group 4

Documentation

Documentation



ABSTRACT

This report on work in progress at Art and Archaeology Technical Abstracts describes the regular and special publications program, the local information management system designed to respond to AATA requirements, and the prospective projects that exist for AATA's participation in this and other developments of the Conservation Information Network (CIN). The collaborative nature of AATA's activities are described in relationship to the other sections of the Getty Conservation Institute's (GCI) Documentation Program, fellow contributing institutions in CIN, and numerous professionals who have been involved in the abstracting and editorial effort for decades.

The development of a local information management tool by the GCI Network staff and its consultants has created possibilities for further cooperative information projects. Such prospective projects as a shared database publication and the development of common terminology through authority files, thesauri, and classification systems are now feasible using common standards, formats, and procedures.

KEYWORDS

Conservation/Abstracting & Indexing Services/Databases

REPORT FROM AATA: COLLABORATIVE ACTIVITIES

Jessica S. Brown
Getty Conservation Institute
4503 Glencoe Avenue
Marina del Rey, California 90292
U.S.A.

Introduction

The GCI Documentation Program supports conservation and related scientific, historical, and other multi-disciplinary cultural heritage research by: 1) collecting and compiling Art and Archaeology Technical Abstracts (AATA), a bibliography of abstracts of the technical literature of conservation published semiannually on behalf of the International Institute for Conservation of Historic and Artistic Works in London; 2) coordinating the project management, research, development, production, distribution, promotion, and training activities of the Conservation Information Network (CIN); and 3) building an outstanding international collection of essential literature in the GCI Library. All three projects interrelate in the collection and dissemination of information on cultural heritage conservation. This discussion focuses mainly on the AATA objectives that have been facilitated by AATA's participation in CIN and coordination with the Network project at the GCI.

The 1987 public launching of CIN [1] began a new era in the provision of information to conservators and other museum personnel for technical-historical research in the conservation of art, artifacts, natural history specimens, architecture, and archaeological sites, as well as the related materials sciences. At present the Network's bibliographic database (BCIN) contains over 130,000 references. These references provide information from over 2,000 journals, plus numerous monographs, theses, unpublished reports, conference proceedings and preprints, and audiovisual resources. Over 10,000 abstracts and literature references are added to BCIN each year. AATA contributes to BCIN and has participated in the development of its format and standards, using the online system to publish the abstracts and indexes in AATA from 1986 through 1989. An in-house microcomputer-based system has been implemented in 1990.

AATA's Regular publications

The regular publication of AATA depends entirely on the abstracts submitted by volunteers within conservation and the related professions. AATA compiles the abstracts sent by an international network of some 200 volunteer abstractors, classifies the materials into the topical and material-based chapter heading scheme, enters abstracts to the local management system, verifies the accuracy of geographic, journal title, publisher, and other "authority-controlled" information, and re-sorts the abstracts into the chapter sections. The abstracts are then submitted to the AATA Editors, based on each editor's area of specialization.

Each AATA Editor reviews his/her section and a meeting follows to discuss abstracts that have raised particular questions. These questions generally pertain to: 1) the relevance of a particular abstract to the scope of AATA overall; 2) specific queries to abstractors regarding treatments, processes, or materials described; 3) the selection of a category within the AATA classification scheme for a particular abstract; and 4) abstracts that require the expertise of a second Editor. One absolute rule among the AATA Board is that any abstract deemed not relevant to AATA's scope by one editor must be reviewed by a second editor. When the second editor does not agree with the recommendation of the first, the entire board discusses and decides upon the abstract.

The AATA Board of Editors has been responsible for the many useful changes introduced in recent volumes of AATA, including the implementation of an enhanced classification scheme for the chapter headings. Chapter introductions are another new feature. Beginning with the second 1989 number, each AATA section provides a description of its contents and relationship to the other sections. It is hoped that the new introductions will make AATA easier for users and more straightforward for contributors.

Besides the 1988 expansion of the classification scheme for architectural conservation [2], AATA's coverage of the technical literature in archaeology has been more clearly defined in 1989-

1990. The following categories will appear in the 1990 volume to provide a structure for improved access to the literature of all conservation-related areas of archaeology:

- 1 Archaeological conservation
- 2 Archaeometry
- 3 Site location and documentation
- 4 Excavation and processing techniques and field conservation
- 5 Site preservation and management
- 6 Geoarchaeology
- 7 Environmental archaeology
- 8 Experimental archaeology
- 9 Archaeobotany
- 10 Archaeozoology

During the coming triennial period, another special development in AATA's regular publication program will occur with publication in the first 1991 number of an AATA supplement on the conservation and restoration of musical instruments. Discussions have begun with the AATA Editors, the International Committee of Musical Instrument Collections (CIMCIM), and the sponsoring editor who will compile the supplement. This will provide a much-needed body of bibliographic information for professionals working with all types of musical instruments.

AATA Special publications

The most important special long-term publication project for AATA is unquestionably the Cumulative Index to Volumes 11-25 (1974-1988), underway since early 1989, with an expected publication date of 1992. In 1988, the AATA Editors formed a sub-committee to define the requirements for the cumulative subject index. A number of these principles for indexing and guidelines for developing terminology are articulated in a late 1989 report of the Managing Editor to the full AATA Board of Editors [3]. To date, a basic list of terms has been developed and classified, using a prototypical classification system and terminology gathered over the past four years. Barbara Snyder, the GCI Microsystems Coordinator, will be discussing the structure and classification of the terminology in a separate paper for the 1990 ICOM-CC Documentation Working Group session. Thanks to the work of the AATA indexing committee, some of the more problematical and ambiguous terms and issues were identified in a series of meetings during 1989.

In the years between now and the 1992 publication of the cumulative index, it is likely that each annual AATA subject index will introduce slight changes and new features. The annual indexes for Volumes 26-29 will be prototypes for the cumulative project and the future annual volume indexes.

The objectives of the cumulative index project coincide with the plans for BCIN. In June, 1989, the contributing partners agreed that AATA and ICCROM would work together in developing common principles for subject indexing in online and print formats. At present, a feasibility study is underway to look at the ways that the bibliographic information gathering and distribution and vocabulary development activities of the GCI Documentation Program and the ICCROM Library might complement one another.

The Local Information Management System

The microcomputer-based information system in use at the GCI is an application, developed by the GCI and its consultants, using a commercially available software package [4]. The system has been developed over the last two years in response to a number of the initial objectives of CIN, as well as the GCI Documentation Program.

Since one of the goals of CIN was to provide contributing partners with a system for local management of the information contributed to and derived from the Network databases, the specifications for a system had to respond to the management and production requirements, notably the dissemination of publications, of all CIN partners. Equally important was the objective of creating a tool to facilitate the exchange of bibliographic information and new findings regarding cultural property, using formats and terminology that could be understood by all practitioners [5]. Given the diversity of objectives to which the system was intended to respond, it has taken an unusually short time to develop the first version. AATA is publishing Volume 27 (1990) from the system.

The local requirements for the AATA production system had to take into account the format and standards for the bibliographic records in BCIN [6, 7]. However, the management and production system for AATA was unique in a number of ways. First of all, as a compilation of abstracts contributed for over 30 years by volunteers within the conservation profession, AATA had to have an online system to track both the periodicals covered and the people contributing the abstracts. Previously these had been managed on index cards. The other CIN partners were using BCIN to manage incoming source documents in their libraries or documentation centers; AATA was primarily managing incoming abstracts.

Thus, while AATA has shared in the overall requirements of CIN to standardize ways of describing bibliographic and intellectual content, as well as physical location information about documents, AATA has also had unique requirements [8]. These include: verifying bibliographic information, often without access to the actual source document; managing information regarding journals received in exchange for AATA, and passed to the GCI Library after publication of an abstract; checking for duplication of abstracts that have been submitted previously to AATA or to BCIN; and preparing CIN information for publication.

This last requirement has led AATA to propose a standardized set of codes for publication of roman-alphabet characters representing over 20 languages, technical and scientific nomenclature, and a variety of type sizes and faces. In the AATA 1990 volume a newly developed generic coding system, based on the Chicago Manual of Style for Electronic Publishing [9] has been implemented for AATA publication. It is being proposed to CIN as a standard for database information that is published in hard copy.

Finally, the system has also provided a mechanism for the AATA staff to manage, classify, and prepare the abstracts in-house for expert review by the AATA Board of Editors. The local system will be used for the 1990 volume subject index.

Future Prospects

Some of AATA's most difficult bibliographic problems have been solved precisely because we are sharing information about documents among the CIN partners. Moreover, the development of the Network frontend has provided a tool for analyzing and sharing the abstracting and indexing effort, and eliminating unnecessary duplication of effort. The local information management system has allowed AATA and ICCROM to adopt common forms, procedures, and tools for abstracting and indexing, with many possibilities for greater coordination of activities.

It is hoped that other collaborative possibilities will also be available, such as access to the terms and tools of the Getty Art History Information Program's Art and Architecture Thesaurus, in exchange for contributions by ICCROM, AATA, and the other CIN partners. As we are all aware, this is a project that requires a long-term commitment to building and maintenance. A thesaurus for conservation information management, whether for subject indexing, treatment reports, or reference materials management, is a formidable undertaking.

It is thus particularly important to gather ideas from an array of potential participants in a thesaurus project since any or all of the following types of information may be recorded: physical description of visual material, names of people, places, objects, sites, analytical processes, products, periods, and general concepts.

Assuming all plans proceed on schedule, AATA will have several significant accomplishments in the next triennial period, including publication of the first cumulative subject index to AATA in nearly twenty years and participation in the development of a rudimentary thesaurus. It is hoped that significant further progress will have occurred in bringing together the abstracting and indexing efforts of the GCI, ICCROM, and others involved in providing secondary bibliographic information to those engaged in conservation research and scholarship.

Conclusion

Since AATA began database publishing in 1986, numerous possibilities for sharing and collaborating in gathering cultural heritage information have emerged. In the 1990s it is likely

that the trend toward growing collaboration among information gatherers will result in further opportunities to coordinate access to the literature--as well as to new, previously unavailable information resources in the field. Once the standards for structuring and providing information are well established, new opportunities for developing information resources will present themselves. The future of information access for the cultural heritage community looks promising indeed!

References

1. J. Perkins, H. Jelich and R. Lafontaine, "The Conservation Information Network," (Paper delivered at the Eighth Triennial Meeting of the International Council on Museums Committee for Conservation, Sydney, Australia, 1987) Preprints Volume I, 255-260.
2. G. M. Helms, "Architectural Conservation," in AATA, Volume 26, Number 2, p. 77.
3. "Managing Editor's Report: AATA Indexing Project," an internal working document from the Managing Editor to the AATA Board of Editors (November 28, 1989)
4. Advanced Revelation (copyright 1988) is a software package produced by Revelation Technologies, Inc., Seattle, Washington, providing a tool to manage information in a relational database environment.
5. B. Snyder, "The Conservation Information Network Frontend System," paper presented to the Third Annual Conference of the Museum Documentation Association entitled "Sharing Database Resources," held September 14-18, 1989, York, England.
6. Conservation Information Network: BCIN Data Dictionary, Version 1.0, prepared by the Data Management Section, Documentation Program, Getty Conservation Institute, based on the work of the Bibliographic Database Content Review Board (October 1, 1987)
7. Conservation Information Network: User's Guide, Version 2.0, prepared by User Services, Documentation Program, Getty Conservation Institute (June 1, 1989)
8. Functional Specifications: AATA Management and Production System, Working Document Version 1.0, prepared by Microsystems, Documentation Program, Getty Conservation Institute (June, 1988).
9. "2. Generic Coding of Electronic Manuscripts," in Chicago Guide to Preparing Electronic Manuscripts: for authors and publishers (Chicago: University of Chicago Press, 1987), pp. 43-84.

ABSTRACT

This paper introduces the use of management and information systems analysis for conservation. General root definitions and conceptual models are suggested for museums and conservation. Further management concepts are employed to draw up mission statements and aims, and finally to arrive at some general performance measures for conservation. The analytical techniques and generalised models described may be used to design management information systems for different types of museum and other conservation organisation.

KEYWORDS

Management, information system, systems analysis, performance indicator, critical success factor, objective, mission statement, conservation record.

MANAGEMENT INFORMATION FOR CONSERVATION

Suzanne Keene
Head of Conservation
Museum of London
London Wall
London EC2Y 5HN
U.K.

Introduction

The conservation of collections means in a broad sense their preservation and maintenance in good condition. Conservators themselves are interpreting their role more widely; no-one working primarily on interventive treatment can be unaware of what brought about the need for treatment. Museums, certainly those in America and the U.K., are at the same time being made more accountable for the upkeep of their primary resource, often a publicly owned asset, and for the effective use of resources.

But how do we measure whether we are succeeding in preserving the collections effectively? Conservation managers are well aware of the difficulty of gauging productivity - one object may take an efficient conservator a year to treat; the next, half an hour. Perhaps we treated a thousand objects last year, but were they the ones most in need? Are the ones in the worst physical condition in fact those of the highest priority? In fashionable management terms, what should we use as PERFORMANCE INDICATORS: how do we measure success?

We share this need for information on success with managers of many other kinds of organisation and organisational affairs (1). The spirit of the times brings the need, the increasing use of computerised records systems, indeed any systematic recording system, the opportunity, to generate quite sophisticated management information.

Tools for Analysing Information

Management studies often include a consideration of information for managing (2). Allied to this field of research is information SYSTEMS ANALYSIS, the orderly analysis of an organisation's use of and need for information, often undertaken in order to design computerised information systems of all kinds.

The Systems Approach

This rather general term covers a variety of related methodologies (1). They have in common a view of organisations and their functioning as groupings of inter-related and inter-dependent components or sub-systems, having some common, overarching purpose. So-called 'open' systems, such as museums, respond to pressures and influences from outside their boundaries. The systems approach to management, used wisely, can be "a means of understanding situations" (3).

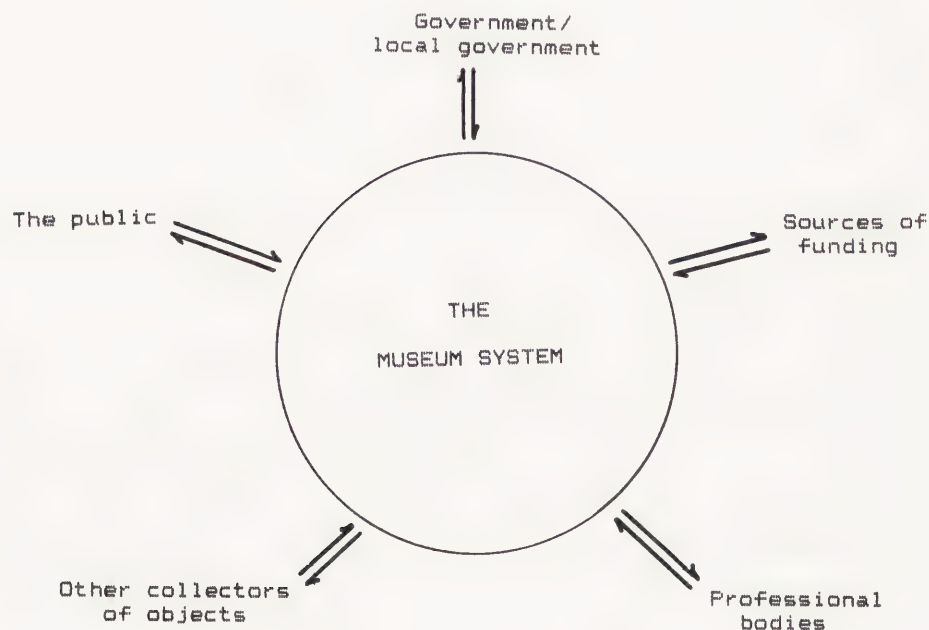


Fig.1 A museum system and its context

The systems approach is related to, but not exclusively concerned with, information systems analysis. A particular branch known as **SOFT SYSTEMS ANALYSIS** takes the approach of learning, in partnership with the organisation, what are its aims and fundamental views. Originated by Checkland (4) and well explained by Naughton (5), it is especially helpful in elucidating how exactly an organisation needs to use information. Management information systems are found to be difficult to design successfully (6), because the more commonly used techniques of **HARD SYSTEMS ANALYSIS** concentrate on the mechanical procedures of the organisation, and so miss the real point of what constitutes success.

Some Tools from Soft Systems Analysis

Museums can be defined as systems, and described in systems terms; and the preservation of the collections will be found to be carried out by one or more sub-systems of the system. In contrast, the main system in a private conservation firm would be the firm itself. Both systems and sub-systems may in turn have constituent sub-systems.

There is a systems law which states, in general terms:

The purpose of a sub-system cannot be defined without first defining the purpose and objectives of its parent system (1).

It is common sense (and common experience) that objectives for conservation cannot be defined in isolation from the objectives of the main organisation. A first step in designing management information is to define objectives, but this cannot be done for conservation until we have examined the purpose of the museum or parent body itself, to determine its preservation objectives.

This gives rise to another point, that soft systems techniques, indeed any successful systems analysis, can only be fully carried out with the help and co-operation of those involved, and those in charge of them. That is, the people who own the system must help to do the work of designing it. This ensures that the analyst's ideas are in fact relevant and useful; that the point has not been missed; and also teaches the users about the system, and even about the organisation (6).

The first technique to be introduced is the **ROOT DEFINITION**: a precise description of the processes which are fundamental to the organisation, or part of the organisation, in question. One possible root definition of a publicly owned museum might be:

ROOT DEFINITION OF A MUSEUM SYSTEM

A publicly-owned system in which professionals are employed to collect, preserve and research objects which are of value to people because of their historic, ethnic, or aesthetic qualities, and to use these in the transmission of ideas, concepts and insights through display, publishing, lecturing, or other public events.

Next, what would be a **RELEVANT SYSTEM** for a museum? A relevant system is a meta-system, an abstract view of the essence of the relevant part of the operation. If the preservation of the collections is what we are leading to, then this must be a focal point.

For example, the basic processes of a factory making shoes or any other commodity for sale might be diagrammatically shown thus:

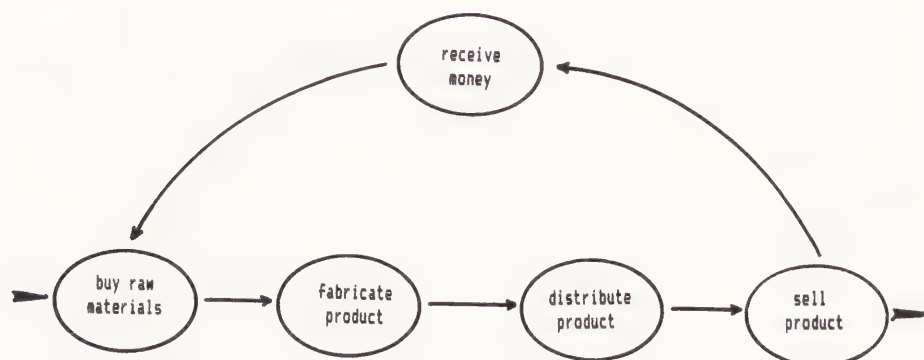


Fig. 2 A relevant system for a production company

A relevant system for a museum might be:

RELEVANT SYSTEM FOR A MUSEUM

A system in which a non-renewable, intrinsically valuable resource is acquired, maintained and enhanced for the future, and used and re-used without deterioration, in conjunction with knowledge and ideas, to transmit ideas, concepts and insights about culture or history to the general public.

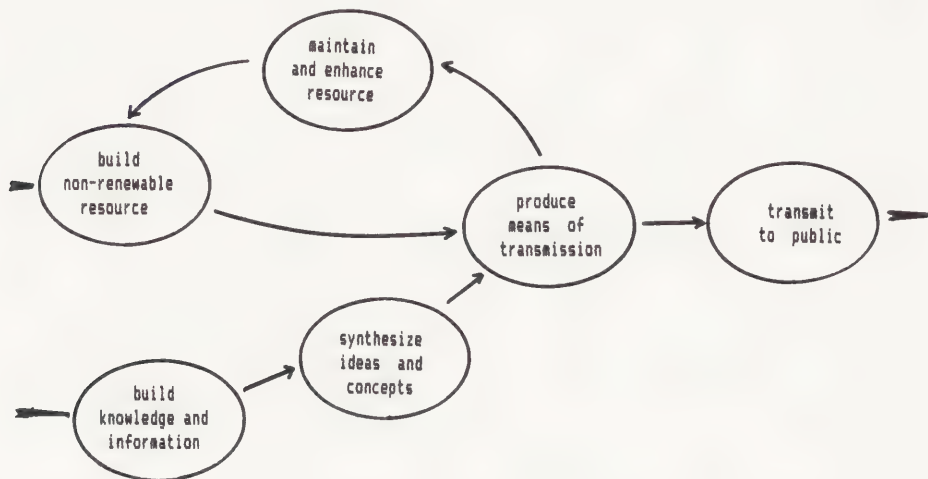


Fig.3 A relevant system for a museum

Though they are very broad approximations to reality, the contrast between the production company and the museum is clear. In the former, goods are fabricated and pass out of the system to be sold. In the latter, the basic resource is non-renewable, and its maintenance is part of the central operation of the system. Furthermore, both a physical resource and knowledge and information about it are necessary to make the 'product', which is in fact ideas, concepts, information and entertainment.

The Conservation Sub-System

The everyday view from a conservation department suggests many relevant systems for the conservation sub-system, for example:

- ... to keep the collections in good condition
- ... to treat and restore objects
- ... to minimise the number of objects that need to be treated (because they are all in good condition)
- ... to make sure that the care of objects gets enough resources
- ... to set and apply standards for the care of objects.

However, the abstraction of the museum relevant system helps to define the relevant system that is needed for the care of the collections (which we may call the conservation sub-system):

A RELEVANT SYSTEM FOR CONSERVATION

A sub-system to maintain a non-renewable and intrinsically valuable resource, and to prepare it for use and re-use as the medium for transmitting ideas, concepts and information....

Missions and Objectives

We now move on to the field of management studies. The following concepts are well explained by Kovach (7). First is the MISSION STATEMENT. This is a concise statement which expresses the primary and basic objective of the organisation. Mission statements will vary from museum to museum: a static collection of pictures will need very different objectives from a working museum of rural life. However, nearly all museums will have collections and their preservation at the centre of their activities, as international definitions of museums make clear; i.e., they will need a conservation sub-system of some kind. A generalised mission statement for a conservation sub-system might be:

A MISSION STATEMENT FOR CONSERVATION

To maintain and enhance the historical and physical integrity and visual quality of the collections through the effective use of staff and other resources to set standards, provide advice, and treat and examine objects.

The next question in moving towards defining the management information we need must be, what do we intend to aim at in order to succeed in our mission? The museum might have some general aims such as these for its conservation sub-system:

1. To maintain and improve the physical condition of the collections so that standards set by the museum for their condition are met.

Note: It may not be an effective use of resources to maintain every item in the collections in top exhibitable condition. Indeed, sometimes untreated objects may constitute a better source of evidence than treated ones. It may be better to set a basic standard below which no object should fall.

2. To maintain the historical integrity of objects in the collections.

Note: Unless the objects are the 'real thing' they cannot play their proper part in transmitting ideas, etc. The kind and degree of restoration required need to be known separately from maintaining physical condition.

3. To prevent damage to and deterioration of the collections in storage, on display, in transit, or during handling or use.

Note: By far the most effective use of resources to maintain condition is to prevent deterioration. Even if all objects are not brought to peak condition they must not deteriorate.

4. To ensure the excellent visual quality of objects when they are displayed.

Note: This is needed to ensure that objects can effectively transmit their 'message' of information, concepts, etc. 'Excellent visual quality' will mean tactful conservation of what is genuine, together with sufficient restoration to ensure physical safety and to clarify the nature of the object, without interfering with the transmission of the object's messages about being genuine and old.

5. To provide a source of expert and accurate technical advice on all matters relating to the care and physical nature of the collections.

Note: As the causes of deterioration become better understood, and the possibilities of sophisticated techniques of scientific examination more available, the museum needs accurate scientific advice on how to apply technical advances. Advice will also be needed for the purposes of authenticating prospective acquisitions.

6. To contribute to the analysis, understanding, authentication and accurate recording of objects.

Note: Conservation involves an intimate and detailed understanding and observation of objects, and often scientific examination as well. This must be added to the general pool of information about objects.

7. To make the most effective use of resources for the care of the collections, and to promote this in other areas of the museum's operations.

8. To ensure high quality and professionalism in all activities.

Note: General objectives such as the last two might well be set for each of the operational divisions of a museum.

To make progress towards these general aims, they must form the basis for more specific objectives set for a year, or a few years, ahead, and be regularly reviewed and revised. For example, in pursuit of maintaining and improving the condition of the collections the immediate objective might be to treat all the highest priority objects in the prints and drawings collection within the next two years. Here, there is not only an objective but also a target: to hit the bullseye we need to complete a particular task within a specified time. However, just as a production company might need to measure ongoing progress for a major general aim, to operate profitably, so it will be useful to devise measures for these general conservation aims.

It needs to be stressed again that, just as the users of the system need to take part in the analysis, aims and objectives need to be designed with the help of the people who will be undertaking the work, and of course with managers. It will be little use devising a mission statement that is at odds with the rest of the organisation.

Measures of Success

It is now possible to start to devise PERFORMANCE INDICATORS, the measures we want. To do this, we need to take each objective, and ask the question, "How do we measure progress?" (6). For the purposes of management information, the answers must only concern things that can actually be measured; some aims may not be measurable. It will often be helpful to ask a preparatory question first: "What must we do in order to succeed?" - sometimes known as the CRITICAL SUCCESS FACTOR.

CRITICAL SUCCESS FACTORS AND PERFORMANCE INDICATORS FOR CONSERVATION

<u>Objective</u>	Critical success factors: <u>What must we do?</u>	Performance indicators: <u>How do we measure progress?</u>
1. Maintain and improve the physical condition of the collections	Know the current and past condition of the collections	* Ascribe grades for the condition of objects, and survey to establish how many in each at intervals * Analyse numbers of objects treated by condition grading
2. Maintain the historical integrity of objects in the collections	Know what constitutes 'historical integrity' for each object	* Record curatorial judgements on whether treatment achieved desired results
3. Prevent damage to the collections	Know what damage and deterioration is occurring. Set environmental standards that will not cause deterioration	* Numbers of objects damaged * Monitor environment, pests, etc. to determine if standards are met
4. Ensure excellent visual quality of objects in displays or photographs	Clean, repair, conserve all objects needing it	* Did all objects needing treatment get it in time?
5. Provide a source of expert technical advice	Keep abreast of current work	* Enquiries from other institutions
6. Contribute to the analysis etc. of objects	Record and make available the results of analysis and observations	* Published observations (catalogues, etc.)
7. Make the most effective use of resources	Plan work effectively Direct work to top priority objects. Monitor productivity Monitor costs	* Objects worked on for an even vs. objects used. * Overtime worked. * Numbers of objects worked on by priority rating. * Number of objects worked vs. target, or average over a period. * Use of time, e.g., by %. * Cost of projects and activities
8. Ensure high quality and professionalism	Acquire and maintain necessary skills. Develop effective treatments. Meet other measures, targets and objectives.	* Courses attended. * Papers published. * 'Lifetime' of treatments.

This list is neither inclusive nor proscriptive. There is other management information that might be useful, too - for instance, about staff turnover and amounts of sick leave. It gives an indication of the sort of information that would prove useful in managing the preservation of collections, but every museum will need to draw up its own objectives, which might differ widely from these.

Bare statistics on numbers of objects treated, though they have their place in work management, are shown to have severe limitations in the context of success in preserving the collections. To quote a journalist writing recently about the English health and social services, "what matters is not the level of activity of these agencies, numbers of letters written or patients seen, but the standard of health and the level of poverty". It would actually

be more useful for measuring performance in preservation to count numbers of objects that did not need treatment! Much of the information for these measures will be collected during the normal recording of objects worked on, or in other conservation activities. For some measures, all that is needed is a more sophisticated analysis of the data, or sometimes a small additional piece of information. For example, most condition surveys of collections include a conservation priority rating. To know if we are working on the objects that need it most, we need to know what was the priority rating for the object as well as that it was treated last month. If, in effect, we crossed it off the list of objects needing urgent treatment, this can definitely be counted as progress.

Sometimes a more sophisticated view needs to be taken. To arrive at a true priority for work on an object, that is, to be sure that conservation resources are being used most effectively, a curatorial assessment of importance needs to be overlaid on its conservation priority. We ought to be working on those objects which have the highest priority in both conservation and curatorial views. Every museum will have its particular treasures.

Measuring performance in the context of objectives can lead to unexpected insights. For example, many conservators feel that work is too much directed towards the display of objects, not the remedial work that the majority of the collections requires. But an object worked on can count towards several different objectives:

- To prepare it for exhibition
- To add to knowledge about it (learnt in the course of treatment)
- To maintain its historical integrity (misleading restoration removed)
- To contribute to its accurate recording (it was also photographed)

If the organisation is serious about the effective use of resources, it will take advantage of the possibility of 'gearing up' the effects of its work. An exhibition could, for instance, be built around a part of the collections which needs better conservation. Curators often select the objects in best condition, trying to make the least demands on conservation, but sometimes it would be better to select those needing the opportunity to work on them.

Reviewing and Adapting

Systems are dynamic, and must respond to outside change. Management information systems serve the purposes of the larger system. To remain effective, a further step must be to review and revise them at intervals. Is the information being provided really what is needed? Was the information system correctly designed? The team approach needs to be continued, to maintain and improve it.

Conclusion

Few conservators feel that every piece of work they do counts towards a known objective. We often feel torn by conflicting priorities - to spend time on preventive conservation in stores; or on contributing to exhibition design; or on treating objects: to treat an object due to go out on loan; or one which we know to be falling apart. Conservation managers, too, are asked to supply figures on work done which seem to them somehow to miss the point of what they are trying to do. To counter these problems, we do indeed need to measure what we are doing - but in the light of an understanding of how the system works, and within a clear framework of aims and objectives which set out why the work is being done.

ACKNOWLEDGEMENTS

Within the Museum of London my thanks go to Dave Evans, Records Officer, for long and fruitful discussions about conservation information; to Max Hebditch, Director and Valerie Cumming, Deputy Director, for encouraging work in the Museum on information and systems analysis. I also thank Alf Hatton, at the Institute of Archaeology for supervision and encouragement, and the Office of Arts and Libraries, for supporting part of this research.

1. Charles B. Handy, Understanding organisations (Harmondsworth: Penguin, reprint 1981). p.323 and other indexed references.
2. Wendy Pritchard, "What's new in organizational development", in Planning and managing change, ed. Bill Mayon-White (London: Harper & Row, in association with the Open University, 1986), p.132.
3. Geoffrey Vickers, "The poverty of problem solving" in Planning and managing change, ed. Bill Mayon-White (London: Harper & Row, in association with the Open University, 1986), p.94.
4. Peter Checkland, Systems thinking, systems practice (Chichester: John Wiley & Sons, 1981).

5. John Naughton, Soft systems analysis: an introductory guide", in Complexity, management and change: applying a systems approach, Course T301 Block 4 (Open University, 1983).
6. Leslie Wilcocks and David Mason, Computing work (London, Paradigm, 1987), Ch.4.
7. Carol Kovach, "Strategic management for museums", The International Journal of Museum Management and Curatorship, 8 (1989), 137-148.

Abstract

Revisiting the goals and activities of the Conservation Information Network three years after its release to the conservation community reveals a vital and dynamic information service. A crucial test for its future viability will be the success of its transformation from a heavily subsidized venture to one where substantial income is generated by subscribers' use of the service. This paper examines a context for the Network's evolution and offers an optimistic scenario for its future.

Keywords

CONSERVATION, DOCUMENTATION, INFORMATION NETWORK, DATABASES

Conservation Information Network: The Getty Conservation Institute's Evolving Role

Kathleen McDonnell
The Getty Conservation Institute
4503 Glencoe Avenue
Marina del Rey, California 90292 U.S.A.

Introduction

The proliferation of information technology in the last 20 years has magnified the perceived value of information in many institutions, including those responsible for art and cultural heritage. The ever increasing accessibility of information has created an atmosphere where documentation centers have become crucial components of all enterprises and decision makers now expect immediate access to information. These expectations in turn promote the continued gathering, organizing and dissemination of increasingly large amounts of information. And as this quantity grows, so too does the pressure to ensure that the information made available is relevant and reliable. The conservation profession has taken on this challenge with vigor and a creative spirit.

There is general agreement that information technology is more than the computer tools most often used to implement electronic information systems. Conservation professionals who need to manage information must embrace its entire infrastructure. Pioneers in the application of information technology to conservation have addressed many components of this infrastructure, including data modeling [1], standards [2], telecommunications [3], terminology [4], systems analysis and design [5], and thesaurus construction [6]. Ultimately, success in these areas will require long-term commitment, coordination among organizations and countries with conflicting mandates and laws, and persistence despite rapidly changing technical contexts. Even with these barriers, conservation professionals continue to make progress.

The Conservation Information Network (the Network), an initiative of the Getty Conservation Institute (GCI), is the product of over three years of coordination among seven organizations in five different countries [7]. Background on the Network and its development has been presented elsewhere [8]. The Network provides the conservation profession with a communications facility for informal information exchange and access to that core of information believed to be fundamental to the practice of conservation. Currently, the Network consists of an electronic messaging system and online databases containing information about materials used in conservation, bibliographic references and abstracts of literature relevant to conservation research and practice, and information about manufacturers, retailers and distributors of supplies and equipment for conservation.

For the Network to have grown to what it is today, it was necessary to confront information technology's infrastructure and to challenge the barriers that inhibit international collaboration on information exchange. Experiences of the Network in these areas have applicability beyond its electronic databases. In fact, many of the accomplishments and remaining challenges are equally pertinent to the development and exchange of any information, regardless of its storage and processing medium. Data models, terminology and standards (to name just a few) are fundamental to information management whether it is encompassed by a computer or a metal filing cabinet.

Future Directions

The GCI Documentation Program was conceived in part to manage the development of the Network. The Program's overall mission, however, is much broader. By increasing access to information, by coordinating existing resources to improve information standards and utilization, and by creating new strategies for managing information, the GCI intends to address a very wide spectrum of documentation issues.

The Documentation Program has played a substantial management role in the development and implementation of the Network databases. That role is continuing as operational and maintenance activities predominate and is characterized by: a) management oversight of systems support and operations; b) administration of registration, billing, correspondence, documentation, training, and user support; c) continued development, refinement, and coordination of partner contributions to the databases' content and structure; and d) development and implementation of a microcomputer application [9].

This application was designed to improve the efficiency and quality of contributions to the bibliographic database as well as to provide the Network partners with the ability to manage their library collections and publishing activities locally.

As the Network's database development activity approaches stability, the Documentation Program will broaden its efforts and propose new information projects. However, in order for GCI to engage effectively in other areas of conservation documentation, it will be necessary to adopt new techniques for managing the Network. One obvious strategy would include transferring support and development functions for the databases outside GCI and retaining only the management oversight responsibilities in-house.

There is likely to be an extended transition period associated with moving Network support outside the GCI. The early stages of this transition will be characterized by: completing a cleanup project for the bibliographic database; re-examining the content and structure of information about materials used in conservation; stabilizing the structure of the suppliers database; reorganizing procedures for client registration, account maintenance and billing; restructuring user documentation; finalizing procedures for partner contributions to the databases; completing development and implementation of the microcomputer application; and, at the same time, continuing to market the databases and provide client training.

The completion of the above activities should help to stabilize database support and development mechanisms, a primary prerequisite for moving these functions outside the GCI. This potential move serves two purposes: first, it provides momentum to focus the Network databases on those subject areas and information formats that are best served by a centralized, electronic database environment; and second, it provides the Documentation Program an opportunity to fulfill its original mission of responding to a range of documentation needs.

The role of the microcomputer application in focusing the database context is substantial. As a tool for improving the integrity and reliability of the bibliographic contributions to the centralized database, its implementation will ease the data management responsibilities currently supported in-house. As a tool for local information management, the application opens the door to streamlining the structure and content of the centralized bibliographic database. No longer will the database need to be a cataloging tool or publications environment for partner organizations.

By removing the cataloging, data management and publishing functions from the centralized database, the core information required for efficient access can be reduced and the complexity of the data entry rules simplified. With the microcomputer application performing the publishing and library management functions at partner sites, the central bibliographic database can now serve more focused purposes: to be a repository of bibliographic references and abstracts, to enable users to identify literature relevant to a given topic easily, and to provide adequate information for locating source documents. An important secondary effect of the streamlined database will be reflected in reduced resource requirements for support and maintenance.

Along with new strategies for managing Network support, additional resources will be required to sustain the databases and provide for their growth. From the inception of the Network, it was intended that an increase in the user base subscribing to the electronic services would likewise increase the Network's income. This income would help offset database operation and maintenance costs, partially replacing GCI's initial financing provided to catalyze the launching of the Network.

Given the relatively small conservation community worldwide, it is apparent that the target audience must expand if Network income is expected to contribute substantially to supporting Network operations. The Network Steering Committee has agreed that the content of the databases should expand beyond conservation and include information relevant to all professions concerned with the world's cultural heritage. Already there exist other potential sources of data for the bibliographic database, including the Canadian Conservation Institute's (CCI) recently acquired museology collection. Although the success of this directive is fundamental to the aforementioned transition, its implementation will be challenging in a context of diminishing resources.

Opportunities

When the Network databases have been stabilized and support and development mechanisms have been moved outside the GCI, it will be possible to redirect resources to a variety of other documentation needs. Not only will new projects emerge, but the knowledge and experience gained in the development of the Network will help guide these efforts toward realistic and promising goals.

The development of a thesaurus of conservation terminology has been a goal of the Documentation Program since its inception. The GCI and the Getty Art History Information Program's Art and Architecture Thesaurus (AAT) project are proposing a joint venture to develop such a thesaurus. If the project is approved and funded, it will build upon and integrate existing Getty activities utilizing the structure and procedures of AAT and the early work on facet development and terminology review initiated through the Art and Archaeology Technical Abstracts (AATA) Cumulative Subject Index project. The Documentation Program intends to solicit experienced professionals working in the field of conservation to participate in the thesaurus construction and review process.

In consultation with experts in the conservation community, the Documentation Program will develop a project to address documentation issues surrounding condition reporting and treatment. It is apparent that the work to date in this area is substantial but the need for coordination and integration is pressing. Data requirements, terminology, standardization and information sharing are fundamental to condition reporting and treatment documentation, and the GCI hopes to bring resources to these areas to continue the analysis of information needs, integrate and expand existing specifications and identify opportunities for application.

The Documentation Program has been analyzing the requirements for managing visual materials, such as photographs, slides, computer-generated graphics, and reference materials. Although these activities began as an in-house administrative project, it is likely that much could be extracted and applied to conservation documentation in general.

A feasibility study of a joint publication with AATA and the International Centre for the Study of the Preservation and the Restoration of Cultural Property (ICCROM) will begin this July. Also, commitments to publish an AATA supplement on musical instruments have been made by GCI and by interested individuals in the field.

Conclusions

The impact of electronic media-based information resources such as the Network databases can be appreciated mostly in the developed, industrialized nations and by organizations and individuals with adequate resources for online access to computers maintained in remote locations. In broadening its impact and scope, the Documentation Program must consider the variation in its potential audience. Arts and culture engage a very diverse group of professionals, subject matter that is interdisciplinary, issues that cross national borders and problems that span thousands of years. Such variation suggests that effective creation and dissemination of information requires close attention to its form, as well as its substance. The continued effectiveness of the Documentation Program will depend upon its ability to sustain a broad-based research and development perspective and an collaborative approach to implementation and dissemination.

Reference Notes

1. G. Miles, "Conservation and Collections Management: Integration or Isolation" Paper delivered at the Eighth Triennial Meeting of the International Council on Museums Committee for Conservation, Sydney, Australia, 1987)
2. The CIDOC Committee of ICOM sponsors a Working Group on the Reconciliation of Standards, a group of museum, conservation and information professionals attempting to develop a standard data model for museum information.
3. T. Cooper, "Telecommunications: An introduction" in Computer Technology for Conservators: Proceedings of the 11th Annual IIC-CG Conference Workshop, ed. J. Perkins (Canada: IIC-CG, 1986) 183-189.
4. Museum Documentation Association and The Getty Art History Information Program co-sponsored meeting in 1988 entitled "International Conference on Terminology for Museums."

5. D. Hopkins, "Systems Analysis and Design: An Overview" in Computer Technology for Conservators: Proceedings of the 11th Annual IIC-CG Conference Workshop, ed. J. Perkins (Canada: IIC-CG, 1986) 41-59.
6. "Art and Architecture Thesaurus" (Santa Monica: The Getty Art History Information Program, 1986)
7. The Conservation Information Network is a collaborative venture of the Getty Conservation Institute, the Canadian Conservation Institute, the Conservation Analytical Laboratory of the Smithsonian Institution, the International Centre for the Study of the Preservation and the Restoration of Cultural Property, the International Council on Monuments and Sites, the International Council of Museums and the Canadian Heritage Information Network.
8. J. Perkins, H. Jelich and R. Lafontaine, "The Conservation Information Network" (Paper delivered at the Eighth Triennial Meeting of the International Council on Museums Committee for Conservation, Sydney, Australia, 1987) Preprints Volume I, 255-260.
9. B. Snyder "The CIN Microcomputer Interface" (Paper delivered at the Museum Computer Network Annual Conference, Santa Monica, California, 1988)

ABSTRACT

The Western Archeological and Conservation Center Conservation Database Program manages data in three primary areas: 1) Data Collection (Condition Survey), 2) Data Reporting, and 3) Data Transfer, and it co-exists with the current dBase III+ National Park Service Automated National Catalogue System ANCS program, in order to read specified fields from the ANCS data files for reporting purposes. For application in non-National Park Service collections, another version of this program operates independent of the ANCS database.

Using Data Collection, one can identify both a primary and a secondary material, as well as, select descriptive words relating to condition of the structure, surface, decorative parts, and previous treatment of each material. In addition, a 256 byte memo field allows for written comments. A similar system addresses proposed treatments for the materials. Both condition and treatment are summarized and the estimated treatment hours are tabulated. The reporting feature prints in a standard report format only those characteristics which are recorded.

KEYWORDS

Computer, database, condition survey, documentation laboratory management.

A MULTI-TASK DATABASE FOR
CONDITION SURVEY, CONSERVATION REPORTS, AND LABORATORY MANAGEMENT

James D. Roberts, Conservator
Museum Collections Repository
Western Archeological and Conservation Center
National Park Service; POBox 41058; Tucson, Az; 85717

Introduction

At the Western Archeological and Conservation Center (WACC) of the United States National Park Service (NPS) it was found that there was no useful tracking system for artifact condition and conservation treatments. WACC houses over 1.5 million objects, many in need of one time conservation attention as well as many that need periodic "maintenance". Until now, a comprehensive and flexible computer program has not existed, that is, one specifically written for use by conservators. To address this problem, James Roberts developed the program with Mr. Danny Young of DATAWARE (1814 West Riverview; Tucson, Az; 85745; (602) 798-1646) who wrote SURVEY under government contract. The Multi-Task Conservation Database (SURVEY) was demonstrated at the 1989 AIC Conference in Cincinnati, Ohio.

SURVEY, written in dBASE source code for dBASE III Plus ver 1.1, is self-explanatory and user friendly. The code is accessible in ASCII via any text editor, and can be changed by an experienced programmer. This enables new modules to be written and allows nearly unlimited flexibility to tailor the program to your specific laboratory's needs (e.g. for paintings, paper, etc.). Thus, the Header can also be changed from NPS/WACC to YOUR MUSEUM/INSTITUTION.

The program can generate a number of specialized reports as desired. These include a Condition/Proposed Treatment Report, a Treatment Report, a Maintenance Reminder, and a Materials Usage Report. This feature allows for consistency in the structure and quality of reports generated in the lab. It is also possible to search SURVEY for other specialized requests, such as "all ceramic items with 75% of the sherds that are to be exhibited and require over 50 hours of treatment." Additionally, it is possible to "import" a file into any word processor. Using a word processor allows for explanation or elaboration in the comments sections or as needed.

Database Structure

SURVEY is structured around two databases: survey.dbf and msdata.dbf which correspond to SURVEY, a conservation database, and MSCAT, a catalogue database (this accommodates the arrangement at the NPS/WACC). SURVEY can be used in conjunction with or independent of MSCAT. If records are "insert"-ed into SURVEY, they are automatically incorporated into both survey.dbf and msdata.dbf. The advantage of two separate databases allows for SURVEY to be used primarily for Conservation purposes while still having access to catalogue information in MSCAT which is generated by a different department (Curatorial Services). If one has several database files that correspond to different or private collections, then those *.dbf files must be renamed to survey.dbf and msdata.dbf at the time of use with SURVEY. Revisions in the source code would be necessary to "marry" SURVEY to another catalogue program such as ANCS (Automated National Catalogue System) or another database program such as "R"BASE.

The catalog number links the two databases. At WACC, SURVEY reads 8 characters, 4, left justified and 4, right justified, in order to mimic MSCAT (the system in use at WACC), which uses a National Park Service - PARK acronym plus catalogue number. Although one can use different cataloging systems, the specialized reports searches for all catalogue numbers that have the same specific 4 character, left justified alpha-numeric descriptors. At NPS/WACC, these are park acronyms; in another museum, it could be collections or rooms etc. All 8 digits must be used, e.g. KOLD0001 for object no. 1 in the Koldany collection or 7891 58.1 for accession date: Sept. 1, 1978, object 58.1. This depends on the catalogue numbers for your collection. SURVEY has the capability to build survey.dbf and msdata.dbf to match.

Care must be taken to enter data consistently, especially under the Materials Usage section of the Treatment Data Entry

Screen. For example, consider solvents. At this time, SURVEY can only track the quantities correctly if data is entered 1) in the same order of magnitude, e.g. all "ml" or all "L" and 2) in the same order from a previous treatment, e.g. SOLVENTS (from least polar to most polar). Tracking of quantity begins under the first letter of each column and on each subsequent line. See example below for type of structure for materials and for quantity tracking:

SOLVENTS	WAXES	PLASTICS	BIOCIDES	SOLIDS	AQUEOUS
0.1 L Stoddards		1 tube HMG	0.05 gm	orthophenyl-phenol	
	0.2 Kg	Microcrystalline		2.0Kg	Tannic Acid
		0.03 Kg	PVA		
0.2 L Acetone		0.04 Kg	B-72		.2 L HCl
2.5 L Toluene					

One can use text which extends past the end of the 7 character column. Text characters will translate into the Treatment Report but not the Material Usage Report. The quantities will be added together and appear in that specialized report.

Report Formats

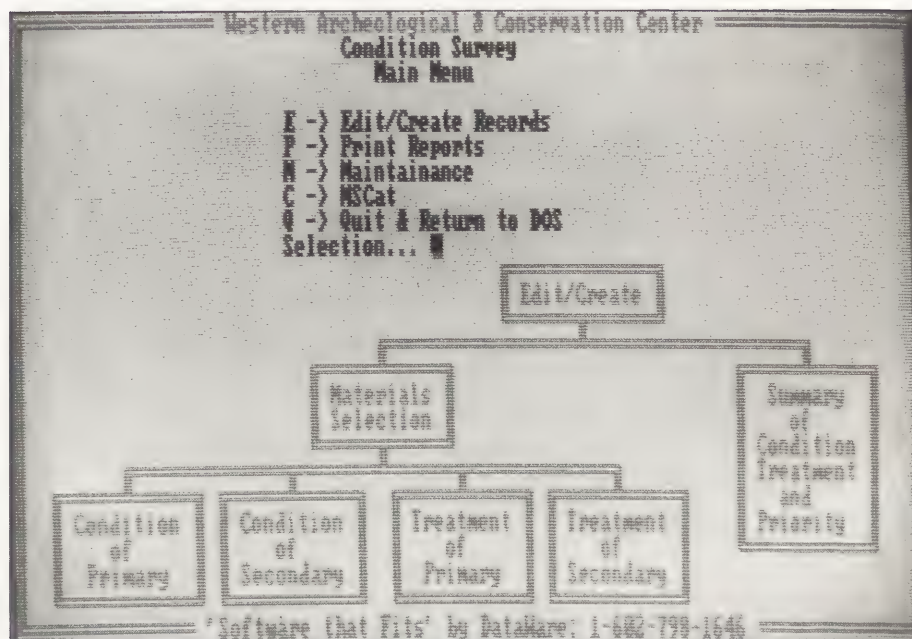
Built into SURVEY are three report formats for Condition Reports, Treatment Reports, and Maintenance Cycle Reports, which are generated in ASCII code. An automatic file name is generated from the catalogue number and the extensions .C, .T, or .M, which refer to the specialized report formats Condition, Treatment, or Maintenance. Each report begins with an Identification Summary, followed by the specific report form requested. The 256 byte comment fields, built into the database, can be expanded "ad infinitum", once the ASCII text files are brought into a word processor, such as WordPerfect 5.0™.

Specialized Reports exist for Maintenance Cycle, Labor and Classification, and Materials Usage, generated between specified dates and for specified collections. The Maintenance Cycle Report also generates a list of those artifacts in need of an after treatment check up. The Labor and Classification Report itemizes the number of items which have been surveyed and treated, summarizing the number of treatment hours estimated verses the number of actual treatment hours. The Materials Usage Report totals the amount of materials used, which can be used as a simple inventory system.

Conclusion

A README file is included with the program which gives the text of the video shown at the Poster Session at the 1989 AIC Annual Conference meeting; a VHS copy of the NPS Video (AIC Demonstration) can be ordered from Film Creations, Ltd; 2021 E. Broadway; Tucson, AZ; 85719 USA for \$16.70.

To obtain a copy of this software, please return one set of the following: 2, 5.25", low density floppy discs, or 1, 5.25", high density floppy disc to the above mentioned author's address. To use this DBASE application, one needs the following: IBM PC or Compatible, DOS ver. 3.3, Floppy Drives, HardDisk (at least 20 MB), and DBASE III+ software (Ashton Tate).



The first screen of the SURVEY program shows a menu of choices and a flow chart of the program.

Western Archeological & Conservation Center
Condition Survey
Edit/Create Records

Catalogued(Y/N)	Photography: (before)
Catalog No. AAAA 0000	B & W Roll Frame
Entry Date 06/30/89	Color Roll Frame
Response Date 01/01/88	Photography: (during)
Conservation No. C88.000	B & W Roll Frame
Arch/Hist/Ethn/Natl/Otr 0	Color Roll Frame
Survey Date 02/02/88	Photography: (after)
Treatment Date / /	B & W Roll Frame
Next Maintenance Date.. 01/01/88	Color Roll Frame
Update.. 0	

ANCS Data:

Name:	Provenience:	Class:
Date:	Dims:	
Cond:	Locn:	
Desc:		

Prob:

Circle Del Edit Ins Locate Material Summary Treatment Quit Point

The Edit/Create screen of the SURVEY program shows the information from SURVEY and the information from MSDATA.

Abstract

Vocabulary control is a commonly accepted practice in the library world and is slowly but surely infiltrating museum documentation practices. The need for precise and standardized terminology extends, however, beyond registration and curatorial functions into the sphere of conservation activities and wherever else conservation-related information is recorded and communicated. While vocabulary lists and thesauri for generally describing and classifying museum objects are moving towards maturity, a project to develop a multilingual and broad-based conservation thesaurus has not yet been undertaken. The Getty Conservation Institute (GCI) has long recognized the need for a conservation thesaurus. Over the past five years, the necessary groundwork has been laid to undertake such a project by identifying vocabulary sources and potential applications and assimilating the experience of contemporary thesaurus projects. This paper is intended to summarize Getty efforts to develop a conservation thesaurus, to outline a recently proposed thesaurus conceptual framework, and to suggest areas in conservation documentation where a conservation thesaurus can be applied.

Keywords

CONSERVATION; THESAURUS;
VOCABULARY CONTROL

Conceptualizing a Conservation Thesaurus

Barbara L. Snyder
Getty Conservation Institute
4503 Glencoe Avenue
Marina del Rey, CA 90292
U.S.A.

Conservation Thesaurus Background

In 1984 and 1985, the Conservation Information Project (CIP), the precursor to the GCI Documentation Program, began to research issues involved with the construction of a conservation thesaurus. A primary source for the CIP was the Art and Architecture Thesaurus (AAT)[1], a Getty project which coordinates and publishes standardized vocabulary of art and architecture terms for use in bibliographic and visual databases and in the documentation of object collections. The CIP and AAT worked to identify categories of terminology relevant to conservation and to propose how these categories might be structured.

It was soon realized that conservation terminology would not simply form a hierarchy within the AAT. Much of the terminology used by conservators overlapped with the AAT. Some of the overlapping terms, however, meant one thing to art or architectural historians and something else to conservators. It appeared that conservators would need certain categories of information such as materials in greater detail and with more technical emphasis than provided by the AAT. Regardless of the foreseen complexities, the benefits of collaborating with the AAT to build a single thesaurus to meet the needs of both historians and conservators were easily articulated.

Efforts to build a conservation thesaurus did not get off the ground, however, until the Conservation Information Network (CIN) was formed. CIN provided the impetus to resume work on the conservation thesaurus by promoting common indexing practices for CIN partners; pooling CIN vocabulary lists and thesauri to build bibliographic, name and subject authorities; and developing a microcomputer system for the management and production of bibliographic information. Once the computer tool for building and interactively using authorities was implemented, a more concrete and urgent demand for a conservation thesaurus emerged.

The spark that actually reignited the conservation thesaurus initiative was the decision by the Art and Archaeology Technical Abstracts (AATA) Board of Editors to build a fifteen year cumulative subject index. The indexing project is spearheading the development of a CIN prototype indexing system and the organization of a critical mass of conservation subject terms. In April of 1988, the AATA Board of Editors Subcommittee on Subject Indexing convened to discuss a conservation thesaurus as a requirement for the cumulative index. Although the AAT could provide the subject indexing project with the principles and standards for establishing thesaurus terms and thesaurus relationships, it did not have an organizational scheme for conservation terminology in place. At the meeting and over the next several months the group drafted a facet-based conceptual framework for the thesaurus.

Conceptual Framework

The AATA subject indexing meeting marks the most concerted effort within the Getty to formulate a conceptual framework for a conservation thesaurus. The importance of a framework cannot be over-emphasized; a comprehensive and rational framework defines the universe of the discipline or subject area which it seeks to represent and provides a skeletal architecture within which terminology can be organized. Once a conceptual framework is established, the work of researching terms and establishing thesaurus relationships can begin. Without a framework, building a thesaurus is much like piecing together a puzzle without ever having seen the picture which the completed puzzle depicts.

The facet model upon which the conservation thesaurus is based was derived primarily from the work of James D. Anderson and his predecessor, S.R. Ranganathan. Anderson, Professor of Information and Library Studies at the State University of New Jersey, Rutgers developed the Répertoire d'Art et d'Archéologie (RAA) and the International Repertory of the Literature of Art

**TABLE I: CONSERVATION
THESAURUS FACETS**

Personality/Entities

Corporate body name
Corporate body/person type
Equipment/tool used in
conservation
Generic origin
Object/Site/Monument/
Specimen name
Object/Site/Monument/
Specimen type
Personage
Theory/Discipline related
to conservation

Matter/Materials

Material of object or
under investigation
Material or product used in
conservation
Material properties

Energy/Activities

Dating
Documentation and
information management
Education and training
Event including natural,
historical, current
Health hazard, safety
measure
Mathematical technique
Objective of Analysis/
Dating
Preventive conservation
technique, process,
policy
Processes, agents, causes of
deterioration
Production technique,
process, tools
Treatment or technique of
conservation
Type/Method of detection,
analysis, examination

Space/Place

Geographic location

Time/Period

Chronologic division, date,
and non-specific time

(RILA) Prototype, a faceted classification and contextual indexing system (FACCIS)[2]. In his report on the prototype, Anderson expressed his concern that "current practice in bibliographic database design and implementation tends to provide extensive structure and definition to elements of document description while knowledge description is frequently relegated to a few, relatively unstructured fields". In response to this concern, Anderson focused on "the representation and manipulation of information related to subject knowledge"[3].

In developing his approach to subject knowledge, Anderson studied the ideas of S.R. Ranganathan, who proposed that knowledge from all disciplines "consists of relationships among and within fundamental categories of concepts"[4]. Ranganathan developed a comprehensive model for organizing information which consists of the following broad categories:

Personality	(or Entity)
Matter	(or Material)
Energy	(or Activity)
Space	(or Place)
Time	(or Period)

The central elements or "facets" of a discipline--people and organizations and the roles they play, the concepts and materials they work with, their activities, and the periods and places with which they are concerned--are the unique manifestations of the PMEST categories. As an organizational scheme, the facets of a discipline can be used to classify a variety of resources and references pertaining to the discipline such as book or visual material collections, subject indexes or thesauri. Anderson and RILA/RAA applied the PMEST strategy and developed a set of facets for the discipline of art history[5] as a subject indexing tool.

Recognizing the value of the art history model and hoping to benefit from the RILA/RAA experience, GCI Documentation staff began work on a conservation facet scheme to form the basis of a conservation thesaurus. Several structures for organizing museum and conservation information were analyzed and essentially mapped into a facet format: the AATA subject classification scheme; the CIN scope statement; the International Centre for the Study of the Preservation and the Restoration of Cultural Property (ICCROM) subject keyword data elements; the ICCROM indexing syntax; the Canadian Conservation Institute (CCI) thesaurus; the Nomenclature for Museum Cataloguing: a System for Classifying Man-made Objects; and the AAT facets and hierarchies. The above sources illustrated the scope and interdisciplinary nature of conservation concerns (e.g. archaeology, ethnology, physics) as well as the types of entities and activities which occupy the conservation landscape (e.g. specimens, materials, chemical processes, equipment). Despite the wide-ranging character of conservation information, the sources overlapped considerably and were reduced to a comprehensive and cohesive set of conservation terminology facets.

The drafting of the conservation facets was timed to precede the AATA subject indexing meeting which took place in April, 1989. It was intended that the facets be reviewed and more precisely defined by conservation subject experts. In fact, the facets underwent the ultimate test of verification against conservation terminology known to be in use. A list of over seven thousand AATA subject terms drawn from the conservation literature was divided among three AATA editors who subsequently "facetized" the terms by attempting to assign them to an existing facet. This process resulted in the modification of facet definitions, the collapsing of facets, and in some cases the deletion of facets. The facets which emerged from this process are presented in Table I.

Each of the facets has a definition which includes the scope of the information it categorizes and terminology examples. The **Equipment** facet, for example, contains terms for equipment and tools used in conservation. Examples are Drying table, Vacuum table, Pounding brush and Quill. The **Production Technique and Processes** facet contains terms such as Engraving, Molding, Casting, and Painting. As a final example, the **Preventive Conservation Processes and Practices** facet groups terms such as Environmental control, Exhibition, Handling, and Shipping.

Potential Applications

CIN frequently receives requests for information regarding the whereabouts of controlled conservation vocabulary. Requests appear to stem from the requirements of two basic applications:

1) providing subject access to reference resources and 2) controlling data values for a particular data element. Either type of application may require fairly general or very specific terms. A bibliographic subject index may be geared towards the general public or specialists. Similarly, an object's condition may be recorded with a general term in the case of a gross object inventory, or with a specific term in the case of a pre-treatment condition report.

Within CIN, a primary application for a conservation thesaurus is in the area of subject indexing bibliographic material. CIN's subject indexing prototype will use thesaurus terms to construct multiple term phrases such as "Air conditioning. Environmental control. Power House Museum. Australia" and "Authentication. Photograph. Electron dispersive spectrometry. Microscopy. 19th century". The appearance of these phrases in a hard copy index will be generated based on rules for ordering and combining terms from the same and different facets. A typical generic phrase structure, for example, would be "Object type: Object name: Object material: Treatment or technique of conservation".

Two features of this approach to subject indexing merit further comment. The ability to construct phrases requires a thesaurus which captures terms as units or concepts rather than as precoordinated phrases or headings; terms can therefore be used as building blocks. Secondly, because each thesaurus term belongs to a facet which represents a central aspect of the conservation discipline, a rational ordering of facets generally results in a rational ordering of terms. The subject indexer is relieved of the time-consuming and often arbitrary task of ordering terms within a phrase. The potential rigidity of automatic phrase formatting can be diffused by providing a mechanism for overriding the format.

Visual material constitutes a second major resource requiring subject access, ranging from treatment photo-documentation to large collections of images, drawings and models. The GCI Library is responsible for a collection consisting primarily of slides, photographs, transparencies and diagrams generated by conservation field projects, laboratory investigations, condition analyses and grant proposals. These materials may be retrieved for purposes of publication, research, project documentation or promotional material, and therefore require flexible yet precise subject access.

Fortunately, the same conservation thesaurus used to index bibliographic material can be applied to visual material. At the GCI, plans are underway to implement the CIN subject indexing prototype as a component of the Library's visual materials management system. As the Library begins to index the collection it is expected to become an important contributor of conservation terminology.

Condition and treatment reporting represents the second type of thesaurus application, that of controlling specific data elements. The typical report includes information on the object/object components' materials; storage requirements; display requirements; condition; previous treatment; and proposed treatment. Each of these elements is a candidate for vocabulary control as demonstrated by the fact that report forms often include checklists of valid terms. Conservation facets, in this context, can be isolated from the rest of the thesaurus to control single data elements. The **Treatment or Technique of Conservation** facet, for example, could guide the assignment of values to the "previous and proposed treatment" elements.

Object facets which are usually assigned by a registrar or curator e.g. Object Type, Object Maker, and Generic Origin are also included in typical condition and treatment reports. These facets are examples which may already be found in authorities such as the AAT but are also required by conservators. By collaborating with a project such as the AAT, the conservation profession can concentrate on terminology which is relatively unique to the conservation discipline and not available from other standard sources.

Conclusion

Although the conservation profession still lacks a conservation thesaurus, the first and possibly most critical step, that of developing a conceptual thesaurus framework, is underway. A scheme which defines the essential facets of the conservation discipline has been drafted and will mature as it is exposed to

the body of conservation information through implementation in bibliographic, visual material, museum collections management, and conservation analysis and reporting applications. A collaborative approach involving a merge with related authorities already in the field could lead to the development of an essential and all-embracing documentation tool for cultural material.

REFERENCES

1. "Art and Architecture Thesaurus", (Santa Monica: The Getty Art History Program, 1986)
2. James D. Anderson, "RAA/RILA FACCIS. A Faceted Classification and Contextual Indexing System for the Merger of Répertoire d'Art et d'Archéologie and Répertoire Internationale de la Littérature de l'Art" (Unpublished report, State University of New Jersey, Rutgers, September 1985 - June 1986)
3. Ibid., 5.
4. Ibid.
5. Ibid., 6-7. (For RILA/RAA facets)

ABSTRACT

The paper analyses the contemporary state of scientific restoration documentation. It considers drawbacks of information search systems existing till now. It tells in detail of the use of a personal computer to process massive restoration documentation, of systematization and unification of all restoration documents. The author reveals the prospects of using a computer in restoration practice. The paper contains illustrative material (print-outs taken from the computer, some new forms of restoration documents, etc.).

KEYWORDS

Information search systems, personal computer, systematization and unification of the restoration documentation.

COMPUTER IN A RESTORATION WORKSHOP

E.S.Soldatenkov
Ingenernaya ul., 4, 191011, Leningrad
State Russian Museum
U.S.S.R.

Introduction

Computers are gaining more and more ground. Today it is probably easier to name these spheres of science, education, medicine or culture where they are not used.

This became feasible, no doubt, due to the appearance of computers of the so-called fourth generation, with their practically unlimited memory capacity, possibility to increase it, simplification of operations, production and sales of inexpensive ready-made data bases and various special programs. And all this is going on against the background of computers becoming cheaper.

As is known, museums did not miss these opportunities. At present electronic catalogues have been established and are being successfully operated in many of them. But till now there have been certain fields of museum activity that were closed to computers. Here is one of them, scientific restoration.

In order to show that the use of computers here is not just a tribute to fashion we would like to speak of pre-requisites of their application in the Painting Restoration Workshop of the State Russian Museum in Leningrad.

Scientific documentation has of late begun playing an increasingly greater role in the restoration, storage and comprehensive study of works of art. A scientific approach to restoration, becoming firmly established in our museum, requires a detailed analysis of the history of an object: previous restoration interference, materials and methods applied, the data of technical and technological investigation, etc. Therefore, such an active workshop as the Oil Painting Restoration Workshop of the Russian Museum, through which over a thousand a year works of art pass on average, inevitably confronts the problem of an optimal organization of the intensively growing system of restoration documentation.

We also had a "manual" information search system with all its numerous drawbacks. Each of the newly arriving for restoration works of art had to be entered in eight different card indices which existed as a one aspect index each to the principal document bank, the 9th "restoration passport" card index, containing the full information. It covered name card indices kept by the names of the authors of art, and by the names of restorers, registration books and the restorers' card indices, condition card indices and other information. Thus, it is easy to calculate that over nine thousand documents were drawn up each year. Such a system could function only by keeping all the eight different entry files. In so doing it was found that their entries duplicate one another for over 50%.

But even this is not the worst. Most awkward was that the system made it impossible to search by a whole series of very important characteristics, for card indices were kept by only one of the characteristics. That is, for instance, in the first card index one could easily find all the works of art that had been restored, in another one (kept by the restorers' names), only those that were done by a certain restorer. In the third one it was possible to find out the condition of a work of art, etc. Thus, the search apparatus to the system was based on just account storage accounting attributes. Any scientific search was out of the question.

Another thing, in the museum there was no general condition card index for all the objects in museum storage. The information on this requisite, determining one of the principal lines of the entire museum activity in general, storage, were "buried" in the inventory card indices of research departments, arranged by inventory numbers and containing up to tens of thousands of cards. We also had such a card index on painting. The establishment of a new museum condition card index, including such, for example, requisites as "the feasibility of transporting a work of art to an international exhibition", or "insurance cost", or, say, "restoration priority", etc., did not seem feasible with the available staffs. And one could not even dream of es-

establishing and periodically correcting such a card index on a regional scale, although the State Russian Museum is the principal methods centre for museums of the Russian Federation. It was necessary to have such a miracle card index where information once entered could be obtained, so to say, "from any direction" and in the maximum possible volume.

And at this point we made a conclusion that it is a computer alone that could solve this problem. But it is a long way to go from a desire to practical results.

The preparatory work started in 1985 and today we believe that two out of three supertasks had been implemented. An electronic catalogue of painting works that had gone through the restoration workshop was established, containing 20 accounting storage search characteristics. Secondly, there was established a data base containing a full description of the condition of these works with 30 more characteristics. The sum total of search characteristics is 50. The bases are unified. A search can be made by any of these characteristics, or by a group of them at once. For example, one can find out what works by Repin and for what reason cannot be sent to the international exhibition in Finland in 1989, or what works of art (by the results of the latest, autumn, prophylactic examination of the museum entire collection) suffer from the so-called 'oil disease'. In so doing this information can be, if so desired, obtained either on the display screen or in a beautifully printed form.

And thirdly, though yet at a working stage, we intend to set up in the near future a unified "Restoration Passport" data base that would include the entire complex of characteristics. In particular it would contain the decisions of restoration committees, the programs of restoration works, methods applied, etc. It is a tremendous job. This base will also be introduced into a personal computer. To do so a new questionnaire form of the restoration passport has already been elaborated. Its draft was published in 1986 in the Proceedings of the Russian Museum for discussion.

The entire work on the establishment of an automatic information search system was performed along several lines at once:

1. First of all, the so-called 'info-logical model of the object sphere' was designed, i.e., a detailed analysis of the existing 'manual' information search system was made, unjustified information duplication was calculated, and the request typology was studied. And, most important, at the first stage a glossary of all restoration terms was compiled, which was also published in 1986 to standardize the unsettled restoration terminology.

2. Forms of new documents were drafted, published and then duplicated. They were all drawn by the so-called 'closed' questionnaire type system, i.e., all information is already entered in them, the restorer has only to tip with a cross what he is looking for. (Restoration terms in them were drawn from the above-mentioned glossary). Being formalized, new documents became data input forms into the computer. This is all apart from the above-mentioned restoration passport, a 'condition description card' and other documents.

3. A special program was drawn up by N.M. Terterov, senior researcher, Russian Museum information department. It should be also noted that standard 'DBASE 3+' was used as the data base.

Working with the operational data base and compiling a new one conform to the idea of establishing a unified computer network for this country's central museums. This was taken into consideration when compiling the program. The workshop personal computer will be linked to the museum master computer through the modems system.

The results of the research works can be seen in the documents annexed to the paper:

1. Painting Work Condition Card. A new form of the document suitable both for computer data input, and for 'manual' documentation systems. The purpose of the document is to formalize as much as possible and reduce the amount of free description, to save the restorers' labour on drawing up documents for acceptance of pictures to international (the card is bilingual) and national exhibitions. The document is characterized by the substitution of a coordinate grid for description topography, by the principle of choice from a number of ready-made answers by the fixation of degradation description terms and by the use the international system of conventional signs when referring to the

- location of degradations.
2. Print-outs of various types of documents from the computer in reply to a request.
- 2.1. The condition card of one of I.Aivazovsky's paintings.
- 2.2. Information label on the reverse side of a stretcher to be fixed when a picture arrives for restoration.
- 2.3. Transfer card of a group of works from the depository to the restoration workshop which assumes responsibility for its safe custody.
- 2.4. List of works of art for an exhibition.
The paper may have annexed slides from the monitor screen explaining the restoration data base and the computer operation.

The State Russian Museum

THE CONDITION CARD

AUTHOR: I.K.Aivazovsky 1817-1900

TITLE: View of Odessa in the Moonlight 1946inv. № X -2201

SUPPORT: CANVASTECHNIQUE: OILDIMENSIONS (cm) 122 by 190

EXHIBITION/COUNTRY/YEAR "Aivazovsky and Artists of His Circle" (Finland'88)

STRETCHER

Movable with crossarm,

inner edge cut, with keys.

a123456

b

c

d

e

f

GROUND

emulsion. Coloured.

Link to paint layer: satisfactory

PAINT SURFACE:

Craquelure and paint layer cracks: Picture scheme throughout the lower and partially the upper half fine-grained craquelure and paint layer traction cracking, particularly noticeable in white lead body areas. At the lower edge medium-grained craquelure areas with small cracks in the paint layer.

Scratchings over the paint layer: in the middle on the painted sky: 8.5 cm; in the lower left-hand quarter: 1.5 cm.

Grime over the paint layer: along the perimeter.

Restoration retouchings: A/1 - 70 sq.cm., B/1 - 2.5 sq.cm., 4 sq.cm, C/3, B/3, C/4 - lay-out by overpaintings.

Varnish cover: yellowed, non-uniform, white splashes on the left-hand side.

Supplements: dent in the lower right hand corner.

p.t.o.

X-2201 I.K.Aivazovsky 1817-1900View of Odessa in the Moonlight canvas 1846 oil 122 by 190Acceptance: № 23976 20.05.88issue: № 24049 21.06.88Restorer: V.G.Grechin Committee's report on acceptance for restoration - 21.03.88

Distributor:
Restorer: V.E.Grechin
Caretaker: P.I.Dashkina

date

Mouth

year

DATE

27

-

12

-

1988

hour

min

sec

TIME

11

:

31

:

07

p.t.o.

X - I.K.Aivazovsky 1817-1900View of Odessa in the Moonlight canvas 1846 oil 122 by 190Acceptance: № 23976 20.05.88issue № 24049 21.06.88Restorer: V.G.Grechin Committee's rapport on acceptance for restoration - 21.03.88

State Russian Museum

INTRA-MUSEUM
TRANSFER CARD

"APPROVED"

Deputy Director, Accounting Storage
and Restoration

" " _____ 199

At safe custody responsibility

Issued: E.S.Soldatenkov

Oil Painting Restoration Workshop

Accepted: P.I.Daskkina

First half of the 19th - early 20th

Century Painting Stock

the following paintings:

1. №-2201	I.K.Aivazovsky	View of Odessa	1846	canvas
	1817-1900	in the Moonlight	122 by 190	oil

Restorer: V.G.Grechin	Restoration Committee's
	(Council's) Report: 21.03.88
	20.06.88

Issue purpose: Return to permanent custody after restoration.

Grounds for issue: Planned work.

Issued:

Accepted:

	date	month	year
DATE	27 -	12 -	1988
	hour	min	sec
TIME	11 :	28 :	37

State Russian Museum
Restoration DepartmentList of Works from
State Russian Museum

EXHIBITION: "Aivazovsky and Artists of His Circle" (Finland'88)
 accompanying restorer: V.E.Grechin executive restorer:
 V.E.Grechin

1. №	-2201	I.K.Aivazovsky	View of Odessa	1846	canvas
			in the Moonlight	122 by 190	oil
2. №	K5-31	I.K.Aivazovsky	View of the Bosphorus		canvas oil
3. №	-1785	I.K.Aivazovsky	Windmill on the Beach	1837 67 by 96	canvas oil
4. №		I.K.Aivazovsky	Russian Fleet in Sebastopol Roadstead	1856 121 by 191	canvas oil
5. №	-10099	I.K.Aivazovsky	Marine Scene. Storm at Sea	1878 47 by 45	canvas oil
6. №	-1200	I.K.Aivazovsky	Neapolitan Bay in the Moonlight	26.8 by 20	canvas on cardboard oil
7. №	-1777	I.K.Aivazovsky	Storm at Aiya Cape	1875 215x325	canvas oil
8. №	-1778	I.K.Aivazovsky	Senator A.I. Kaznacheev's Portrait	1848 116.5 by 81.5	canvas oil
9. №	-1779	I.K.Aivazovsky	Windmills at Sunset	1862 51.5 by 60	canvas oil
10. №	-1780	I.K.Aivazovsky	Ca d'Oro Palace in Venice in the Moonlight	27 by 37	canvas oil
11. №	-1781	I.K.Aivazovsky	Doge Palace in Venice in the Moonlight	1878 34 by 44	canvas oil
12. №	-1783	I.K.Aivazovsky	View of Moscow from the Vorobiov Hills	1848 41 by 50 oval	canvas oil
13. №	-1784	I.K.Aivazovsky	Marine Scene in the Moonlight	1878 213.5 by 148	canvas oil
14. №	-1786	I.K.Aivazovsky	Marine Scene from the Crimean Mountains	1864 122 by 171	canvas oil

15. № -1787	I.K.Aivazovsky	View of Constantinople in the Moonlight	1846	canvas
16. № -1788	I.K.Aivazovsky	Moonlit Night	1849	canvas
			123 by 192	oil
DATE	date	month	year	
	27	-	12	- 1988
	hour	min	sec	
TIME	11	:	34	: 22



Working Group 6

Modern and Contemporary Art

Art moderne et contemporain



ABSTRACT

Whites of Lucio Fontana's paintings of the same period were examined and classified according to the organic and inorganic components of materials - titanium white, zinc white, calcium carbonate in oil and synthetic resin - in connection with their alterations.

KEYWORDS

Scientific investigations, pictorial technique, white paintings.

WHITE PAINTINGS BY LUCIO FONTANA: INVESTIGATION AND SCIENTIFIC EXAMINATIONS

Pinin Brambilla Barcilon
Civiche Raccolte d'Arte
Castello Sforzesco, Milano, Italia

Antonietta Gallone Galassi
Istituto di Fisica del Politecnico
P. Leonardo da Vinci, 32
20133 Milano, Italia

Introduction

This work continues the research begun several years ago concerning the different aspects of the pictorial technique in the works of Lucio Fontana, an experimental artist who was always carrying out research into the different techniques which he used and re-used throughout his career.

To begin with a collection of the painting materials used by the artist was made, in order to obtain some basic data (1). The causes of alteration of the white paints were then investigated in paintings which had mat and glossy materials juxtaposed and were found to be due to the action of U.V. rays on synthetic resin in the paint (2).

The purpose of the present work is to correlate different materials and techniques to their different behaviour and deterioration - on the basis of the results of scientific examinations - in order to determine a classification to use for knowledge and restoration.

The preliminary phase of our work did not follow a chronological order but some reoccurring expressive forms were considered, such as that of "buchi". This kind of paintings concerns supports and nature of colours - and consequently scientific analyses - and leads to considerations and solutions about restoration. We will not here dwell upon the expressiveness of Lucio Fontana's pictorial artistic language, nevertheless we may observe that all the technical means, also the most magnificent, are never decorative but inspired by great wealth of experience.

A number of white monochromic paintings were examined, with mat and glossy materials and also with inclusion of spangles, glass and sand. During our research we realized that mat whites were the least varied. Then we focused our attention on works of the same period and expression, in order to obtain a first classification of this series of paintings. We found similar results in this group. Three examples representative of the works analysed are here reported. Some particular pigments and binding media combinations emerged: a) titanium white and synthetic resin; b) zinc white and oil; c) calcium carbonate and synthetic resin.

Analytical Method

The results of the analysis are shown in Table I. The samples were examined with optical and electronic microscopes. Microchemical tests were also performed. Inorganic substances were identified by X-ray fluorescence analysis using an electron microprobe on sample cross-sections. The examination of organic substance was carried out by specific tests (staining tests) and infrared spectroscopy. Raman spectroscopy analyses are in progress to identify rutile and anatase in titanium white samples.

Results

Inorganic compounds

C1 - "Concetto spaziale 1968" - with spangles and glass
a) homogeneous zone: The pigment is titanium white (TiO₂)
with zinc white (ZnO₂) traces;
b) white particle : zinc white
c) triangular particle: glass fragments
d) rectangular " " "
(Photo 1)

C2 - "Concetto spaziale 1968"
a) white homogeneous sample : zinc white

- C3 - "Crocifissione 1968" - with sand particles and glass
- a) homogeneous zone: calcium carbonate with magnesium carbonate traces;
 - b) translucent particles (Spot 1, Spot 2): glass fragments
 - c) grey particles (Spot 3, Spot 4): sand particles.

(Photo 2)

Photo 1

"Concetto spaziale" (1968), image at SEM. Titanium white matrix, zinc white particles, large glass fragments.

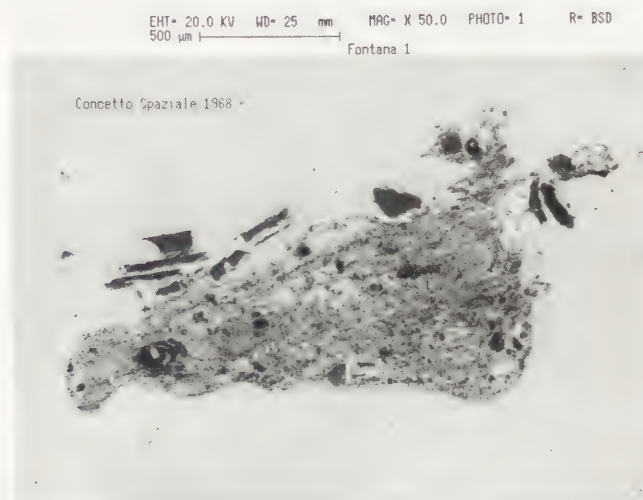
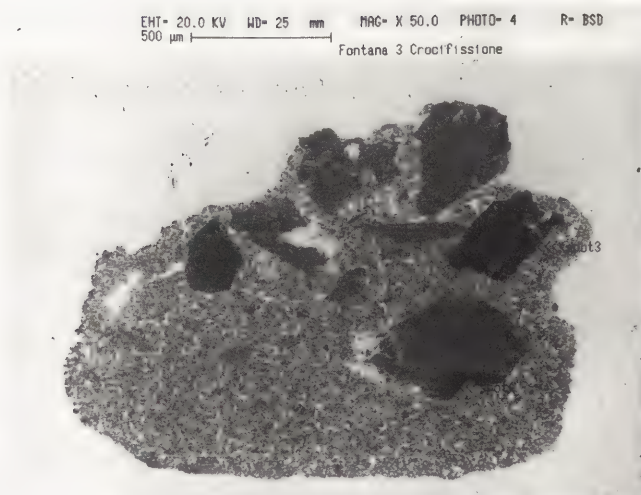


Photo 2

"Crocifissione" (1968), image at SEM: Calcium carbonate matrix, glass (Spots 1,2) and very large sand fragments (Spots 3,4).



Organic media

In sample C1 oil and small quantity of synthetic resin were observed. In Sample C2 the binding medium is oil. In sample C3 synthetic resin is present. Synthetic resin was identified as acrylic by infrared spectroscopy.

Conclusion

We realized that the versatile technique of Lucio Fontana involved preparing his white paint with different materials so as to make it thick or fluid, mat or glossy, according to his expressive intentions.

In some cases (C1) the principal pigment is the titanium white - very fine in texture - mixed with some particles of zinc white. Spangles and glass are included. The medium is frequently oil with synthetic resin. In other cases (C2) a very pure zinc white with oil was used, with a doughy effect. There is the singular use of calcium carbonate (C3) for a sort of mortar where sand is added to spangles and glass fragments. The medium is synthetic resin. The glossy whites seem to vary more than the mat

whites. However, where spangles, glass fragments and sand particles are included, they blacken more because of dust deposits that easily stick to them. The results are still partial and, when completed, can give objective data on the white paintings.

TABLE I
X-ray fluorescence analysis (electron microbe)

<hr/>		
C1 - "Concetto spaziale 1968" - with spangles and glass		
a) omog. zone	(Zn), (Al), Si, Ti"	titanium white, zinc white traces;
b) white particle	Zn", (Si), (Ti)	zinc white, titanium white traces;
c) triangular "	(Na), Si", K, Ca	glass;
d) rectangular"	(Na), Si", K, Ca	glass;
<hr/>		
C2 - "Concetto spaziale 1968"		
a) white omog.samp.	Zn"	zinc white
<hr/>		
C3 - "Crocifissione" 1968 - with glass and sand particles		
a) omog. zone	Mg, Si, Ca"	calcium carbonate, My carbonate traces;
b) trans.part. (Spot 1)	Al, Si", K	glass
c) transl. part. (Spot 2)	Al, Si", K	glass
d) grey part. (Spot3)	(Mg), Al, Si", K, Ca', (Mn), Fe	sand
e) grey part.	(Mg), Al, Si", K", Ca, (Mn), Fe	sand
<hr/>		

Acknowledgments

The authors would like to thank Perside Omena Ribero, fellow at Istituto di Fisica del Politecnico di Milano, for her very valuable contribution in samples microscopical examination and in analysis of media.

References

1. - Pinin Brambilla, Stella Matalon, "Techniques employées par le peintre Lucio Fontana et problèmes de conservation concernant son oeuvre", ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb 1978, (76/6/3).
2. - Pinin Brambilla Barcilon, Antonietta Gallone Galassi, "Some Cases of Colour Alterations in White Paintings of Lucio Fontana", ICOM Committee for Conservation 8th Triennial Meeting, Sydney 1987, Preprints Vol. I, pp. 265-6.

ABSTRACT

The aim of this article is to give a survey of the history and development of synthetic inorganic compounds used as artists' pigments discovered in the 20th century. The history and development of these pigments have been studied from the literature, especially patent literature. The use as artists' pigments will be discussed.

KEYWORDS

Artists' pigments, synthetic inorganic, twentieth century, history.

A BRIEF SURVEY OF THE SYNTHETIC INORGANIC ARTISTS' PIGMENTS DISCOVERED IN THE 20TH CENTURY

Matthijs de Keijzer

Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 8
1071 EA Amsterdam, The Netherlands

Introduction

Three causes led to the development of new pigments in the first half of the 20th century: the war years, the growth of the motor-car industry, and the toxicity of white lead. Zinc chromate was an important pigment during World War Two when many millions of pounds were used for the protection of war equipment. The discovery of phthalocyanine blue in 1934 and later its halogenated derivatives were of outstanding importance, because they were exceptional lightfast, unaffected by acids or alkalis, and in addition, non-bleeding in oils and solvents.

The most significant contribution was titanium dioxide. Introduced after 1918, it met considerable resistance because of its high cost. The share of white lead fell during the period 1900-1945 from nearly 100% to less than 10%. Lithopone's share fell to 15% but the rise of titanium dioxide was spectacular and by 1945 it had captured 80% of the white pigment market. An important consequence was a dramatic fall in the incidence of lead poisoning in the paint industry (1).

Manufacturer's pigment lists of artists' oil colours show that about 50% of the pigments in the A-quality used today and even 70% in the B-quality were discovered in the 20th century. The modern synthetic inorganics: the titanium dioxides, cadmium red and -orange, cadmiumvermilion red and -orange, the cadmopones, molybdate red and -orange, titanium yellow and manganese blue are put on the list of the Standard Specification of Artists' Oil and Artists' Acrylic Emulsion Paints mounted by the ASTM Committee.

History and development

Titanium dioxide, PW 6, (77891), TiO_2

The discovery of titanium took place in 1790 by Gregor near Menachan in Cornwall, England. A year later he communicated to the Journal de Physique the description and the chemical analysis of a black magnetic sand. Little interest was shown until Klaproth in 1795 noticed the agreement between the findings of his investigation of the oxide extracted from "red schorl" from Hungary and Gregor's account of menaccanite. During the 19th century several efforts had been made but for the development of titanium dioxide as a paint they were of no real significance.

The Titanium Alloy Manufacturing Company was incorporated in 1906 and two years later Rossi prepared a relatively pure titanium dioxide and proved its high opacity as a pigment by mixing it with salad oil (2). In 1912 Barton joined Rossi in a systematic research program on the capacities of titanium compounds as pigments, and worked out a method of separating the dioxide from ilmenite (3). In 1914 they found that the addition of calcium- or barium sulphate to the titanium solution facilitated its hydrolysis and gave a composite pigment having a high opacity as any pure titanium dioxide they were able to produce (4). In 1916 the Titanium Pigment Company was organized to produce the products developed by Rossi and Barton (5). The production did not start before World War One, because in 1917 there was a shortage of sulphuric acid. The first composite pigments existed of 25% TiO_2 and 75% barium- or calcium sulphate (Titanox B and C).

The Norwegian Government appointed a committee in order to investigate the possible uses of titanium of the vast deposit of ilmenite of Egersund (1908). In 1909/10 Farup was granted patents covering calcination of ilmenite to produce red or brown pigments and also the process of calcining a mixture of ilmenite and sulphuric acid to produce yellow pigments (6). During 1912/14 a search for other methods of utilization began and led to the titanium dioxide pigments (7). November 1916 the Titan Corporation A/S was founded and commercial scale production began at Frederikstad in 1919 almost simultaneously with the initial output of the United States. To facilitate the commercial development, the American and Norwegian interests, which had worked independently, came together in 1920 and agreed a plan of cross licensing of

patents and mutual exchange of technical information and operation experience.

In the laboratories of the French factory Société de Produits Chimiques des Terres Rares in Serquigny from 1921/23 pure titanium dioxide was developed by Blumenfeld (8). The Blumenfeld-process also needed sulphuric acid and this was an inducement to seek cooperation with a sulphuric acid manufacturer Fabriques de Produits Chimiques de Thann et de Mulhouse. In 1923 this manufacturer started the production. The pigment was available as pure titanium dioxide and in combination with blanc fixe.

The whole titanium dioxide production before 1938 was based on the anatase-modification. One of the disadvantages of the anatase pigment was its poor chalking resistance. In April 1937 Tillmann (Titangesellschaft) patented the manufacture of rutile titanium dioxide and 1938/39 the first rutile pigment came out in Leverkusen (9). Late in the same year it was also made at Billingham on a semibulk scale. War came and the development work on rutile had to be postponed. The first American fine particle rutile appeared in 1941/42. After 1945 the research works on rutile pigments were restarted in Europe and in 1949 British Titan Products produced on large-scale rutile pigments. The rutile production in West-Germany could not be started because the Allies prohibited the use of titaniumtetrachloride. During the war this compound was used as a smoke screen. The production started as late as 1952.

A new episode started in 1957 when Du Pont built a new factory in New Johnsonville and two years later they announced the production of the rutile type by the tetrachloride process. It involves the chlorination of rutile to yield titaniumtetrachloride. The titaniumtetrachloride is purified and oxidized continuously in the vapour phase to produce solid titanium dioxide and gaseous chlorine. This process yields pigments of high chemical purity and uniform quality. The first European factory which produced the rutile type by this process was Britan Titan Products, Billingham in 1965.

Cadmium red and -orange, PR 108, PO 20, (77202), $\text{Cd}(\text{Se/S})$.

With the introduction of the element selenium in the cadmium sulphide molecule colours from light orange (12%) to deep maroon (40%) can be produced. Cadmiumseleno-sulphide is prepared by precipitating cadmium sulphate with sodium sulphide and selenium. The history goes to 1892 when in the German patent 63.558 it was first mentioned but the commercial production did not start before 1910 (10). In 1909 Eibner mentioned a new cadmium pigment consisting of cadmium sulphide and cadmium selenide (11). It was introduced in 1907 by De Haen in Germany and in 1919 it came in general use in the United States (12). In 1919 an improved process was developed by Bayer A.G. which gave a more consistent product and also did away with losses of expensive selenium through volatilization. This method followed the procedure used in the precipitation of cadmium sulphide, but utilized a mixture of alkaline sulphides and selenides. The precipitate is yellow, the red shade develops upon calcining. Calcining must be well controlled, with a temperature of about 300°C employed, if overheated the pigment becomes brown (13). For other manufactures Kittel mentions some patents (14). New developments in the cadmium pigments came in 1961 when Bayer A.G. started with the very pure Cadmopur-red-S-types. In the same year Siegle & Co, GmbH could produce the first types of the FB-assortment (15).

Cadmiumvermilion red and -orange, PR 113, PO 23, (77201), $\text{CdS} \cdot x\text{HgS}$

The cadmiumvermilion red and -orange pigments are the result of well planned research born of necessity. After World War Two the use of the cadmium reds decreased, because of the high price of selenium. The price went up to DM 350,- per kilogram and temporarily to DM 400,-. The reason was a selenium shortage and about 1948 it began to hit the pigment industry. The electrical industry, spurred by increased military and industrial needs for rectifiers was making more and more strenuous demands on the limited supply of selenium, primarily available as a by-product of the electrolytic refining of copper (16). The shortage became acute by 1950 and the Imperial Paper & Color Corporation started a research project in the same year aimed at finding a substitute for the existing cadmium reds. This firm patented (U.S. Patent 2.878.134, July 18th, 1955) a process to develop a new pigment under the trade name Mercadium in 1955. This is a mixed crystal compound of cadmium sulphide and mercury sulphide. It was called Cadmiumzinnobor by Siegle & Co, GmbH in West-Germany in 1956. As an artist's pigment it is of no importance today, because the price of selenium has

fallen sufficiently.

The cadmopones

Cadmium-barium yellow, PY 35:1, (77205):1), $\text{CdS} \cdot (\text{Zn}) \cdot \text{yBaSO}_4$
 Cadmium-barium yellow, PY 37:1, (77199:1), $\text{CdS} \cdot \text{yBaSO}_4$
 Cadmium-barium orange and -red, PO 20:1, PR 108:1, (77202:1),
 $\text{CdS}(\text{Se/S}) \cdot \text{yBaSO}_4$
 Cadmium-barium vermilion orange and -red, PO 23:1, PR 113:1,
 (77201:1), $\text{CdS} \cdot \text{xHgS} \cdot \text{yBaSO}_4$.

It was difficult to produce light yellow and light red tints and also the production of the pure cadmium pigments in the very pale shades was a guarded trade secret. This changed in the 1920's with the discovery of the cadmopones. In the article 'New Cadmium Pigments' Ward says that this pigment was first mentioned in an American patent by Marston in 1921 with about 5% admixture of barium sulphate. In 1927 cadmium lithopones were produced with over 60% barium sulphate. Further developments were carried out in the years 1925/26 and in the autumn of 1926 it was introduced in the United States (17, 18). Cadmopone can be prepared directly in precipitated form by co-precipitating cadmium sulphide and barium sulphate from a mixture of cadmium sulphate and barium sulphide solutions. It contains generally 38% cadmium sulphide and it can be produced at one-half to one-third the price of the pure cadmium pigments. Between the period 1930/40 some patent literature appeared in Europe as well as in the United States (19). The lithopones of the Mercadium pigments appeared on the market after the discovery of the cadmium mercury sulphide pigments in 1955.

Molybdate red and -orange, PR 104, (77605), $7\text{PbCrO}_4 \cdot 2\text{PbSO}_4 \cdot 1\text{PbMoO}_4$

Molybdate red is a synthetic inorganic pigment, the first indication is from mineral origin when Schultze in 1863 noticed that wulfonite (PbMoO_4) had a red colour when it appeared with crocoite (PbCrO_4) dissolved in molten lead molybdate. After cooling a series of salts was set up with a dark red colour. Along the same lines Jaeger and Germs worked in 1921 by fusions at high temperatures. Mixed crystal pigments of lead chromate and lead molybdate were first described in August 1930 by Lederle in a German patent (20) and useful precipitations were later described in the patents of Lederle and Grimm (21). The second American patent by Lederle (U.S. Patent 2.030.009, 4.2.1936) described a process of producing red pigments by precipitating mixed crystals of normal lead chromate, sulphate and molybdate, using a strongly acid solution. The first commercial pigment appeared on the market in 1934/35 in the United States. The Belgian Patent 327.250 (27.2.1937) by Linz described the production of orange and red mixed crystals of lead chromate, lead molybdate and lead carbonate or phosphate. Kittel mentions this process briefly (22). Much research has been carried out to eliminate imperfections: the instability of the crystal structure and the lightfastness. Two patents are of importance: U.S. Patent 2.365.171 (19.2.1944) by Botti and U.S. Patent 2.316.244 (13.4.1943) by Huckle and Polzer.

Titanium yellow, PY 53, (77788), $\text{NiO} \cdot \text{Sb}_2\text{O}_3 \cdot 20\text{TiO}_2$

Titanium yellow is a mixed crystal compound of oxides of nickel, antimony and titanium. It was introduced and produced in 1954 by the Harshaw Chemical Company in Cleveland, Ohio, U.S.A. under the tradename Sun Yellow. Four years later in Europe, Siegle & Co, GmbH and Bayer A.G., followed with the types Nickeltitangelb AN and Lichtgelb 100 (23). In 1965 further developments led to new products: the Rasquin firm developed a lead containing Mineralgelb A and in 1967 Siegle & Co GmbH introduced a chromium containing Nickeltitangelb R (PY 118, 77894).

Manganese blue, PB 33, (77112), $\text{BaMnO}_4 \cdot \text{BaSO}_4$

In the beginning of the 20th century (1907) Bong was the first to produce manganese blue by calcining kaolin, manganese oxide and barium nitrate in the presence of air. The name manganese blue is first mentioned in the patent literature about 1935. Today it is made by calcining mixtures of sodium sulphate, potassium permanganate and barium nitrate to a temperature of 750-800°C in the presence of air. This process was developed by I.G. Farbenindustrie A.G. in 1935 (24). The colour of this pigment is green-blue and is essentially barium manganate fixed on a barium sulphate base.

The use as an artist's pigment

Because of the lack of analytical or other data it is not yet possible to provide a detailed account of the use of these pigments by artists. However, some initial observations can be made. It is uncertain when exactly artists began to use the various synthetic inorganic pigments as artists' pigments. One must consider that a new pigment is not used as an artist's pigment immediately. On the contrary, it is the last link in the chain. In the 1920's the artists were taught to limit their palettes strictly to the permanent inorganics plus alizarine crimson. Fortunately, literature study helps and also the manufacturers are willing to give data and information about the pigments used. Examinations of dated paintings and pigment collections enlarge the knowledge of when and how the pigments came into use.

The first appearance of cadmium red is on the 1918 catalogue of Royal Talens; two types are listed: Cadmiumrood Extra and Cadmiumrood Ordinair. In the first edition (1921) of his book 'Malmaterial und seine Verwendung im Bilde' Doerner treats it in a short chapter. Wehlte complains that it took a long time before one could buy cadmium red as an artist's pigment. He bought his first powder in 1926 in Ivry sur Seine near Paris (25). In the 1930 book 'The permanent palette' Fischer valued this pigment because he placed it on his permanent palette. The author analysed cadmium red in two well-dated art-objects: the Mill panorama of Frans Mars painted in 1946/47 in the Zaansche Schans (26) and in the painting 'Who's afraid of red, yellow and blue III', (1967) by Barnett Newman. Today it is a popular and favourite pigment, and it has replaced vermilion on the artist's palette. Cadmium red and -orange have excellent lightfastness, good alkali resistance but are sensitive to acids and sulphide, are expensive and one cannot mix them with copper pigments.

Fischer writes about titanium dioxide: "Artists have recently been urged to use titanium white. The material is not as good a reflector of white light as zinc white and has a distinctly yellowish tinge. It is permanent to light and air, has great covering power and a good pull. What appears upon the market as titanium white is usually a mixture of this material with much barium sulphate. Such mixtures are still permanent and have great covering power but show an increased tendency to crack and chip off" (27). Soon after the invention of the Blumenfeld-process Société Bourgeois in 1925 and Société Lefranc in 1927 produced titanium dioxide (anatase-modification) as an artist's pigment (28), Messrs Winsor & Newton started in 1934 with the anatase-modification mixed with barium sulphate and after 1965 with the rutile-modification. Royal Talens B.V. began in 1937/38 and only used the anatase-modification. The first dated use of anatase-titanium dioxide was analysed in the painting "The rocking chair" by Picasso (1943) (28) followed by the Mill panorama of Frans Mars painted in 1946/47 in the Zaansche Schans (26). The earliest dated use of rutile-titanium dioxide was analysed in the painting "Compositie 6" (1955/56) by Huszár (29) followed by the painting "Not there, here" (1962) by Newman (28).

Another question is, why anatase-titanium dioxide was initially produced as a composite pigment?

1. It was impossible to produce a pure white pigment, because the iron sulphate could not be removed completely; the colour was therefore yellowish.
2. The addition of finely divided calcium- or barium sulphate into the titanium solution facilitated a hydrolysis and gave a composite pigment having a high opacity as any pure titanium dioxide they were capable of producing.
3. It was feared that pure titanium dioxide, because of its high price, could not compete with zinc white and especially lithopone.

Fischer (30) noticed in his chapter "Palettes of Some Moderns" that the palette of Frederick. J. Waugh (1861-1940) deserves study because he paints with a titanium white (permalba). Permalba is the trade name for a composite white artist's oil colour, introduced in 1920 by F. Weber of Philadelphia, United States (31). Today the titanium dioxides are the whitest pigments, are chemically inert, have excellent covering power and are non-toxic.

The cadmopones are just as permanent, but are less powerful in tinting strength than the pure cadmium products. The cadmium-barium

types are used in most artists' colours; the expensive pure cadmiums are used in the top-grade lines. In the painting "Compositie 6" (1955/56) by Vilmos Huszár, cadmopone yellow was analysed by X-ray diffraction (29).

Truely speaking molybdate red and -orange are of no importance today. It was found on two pigment lists; Schmincke & Co (Zinnoberon) and Messrs Winsor & Newton (Chrome Orange, lead chromate mixed with lead molybdate).

Titanium yellow has a good lightfastness, a moderate high strength and one can compare it with Naples yellow. It can be used in all techniques and is favoured over Naples yellow because it is non-toxic. The colour of Nickeltitangelb R corresponds with that of yellow ochre.

Manganese blue replaced cerulean blue, because its green-blue tint is much purer, especially when mixed with a white pigment. It is also favoured over cerulean blue because of its economy. Manganese blue has a value in painting bright skies. It has a high lightfastness. Royal Talens B.V. placed it on the pigment list in 1937 (32).

Bibliography

1. H. Brunner, A History of Technology, The Twentieth Century c 1900 to c 1950, part 1, chapter 23, (Oxford: Clarendon Press, 1948), 591-592.
2. J. Klein, H. Rechmann, "50 Jahre Titandioxid Pigmentindustrie, Versuch einer Chronologie ihrer wirtschaftlichen Entwicklungen", Farbe und Lack 73, no 5 (1967), 417-424.
3. Rossi, U.S. Patents 1.184.131, October 1911, 1.205.267, November 1912.
4. Rossi and Barton, U.S. Patents 1.106.406, November 29th, 1912, 1.106.410, February 6th, 1913.
5. Barton, U.S. Patent 1.205.144, 1916, British Patent 105.645, May 9th, 1916.
6. Farup, Norwegian Patents 19.978, February 15th, 1909, 20.625, February 15th, 1910, German Patents 242.271, 1909, 260.906, April 28th, 1912, Jebsen, Norwegian Patent 21.693, February 25th, 1910.
7. Farup, German Patent 276.025, July 2nd, 1913.
8. Weizmann and Blumenfeld, British Patents 203.352, 1922, 209.441, July 12th, 1922, 210.033, July 12th, 1922, 255.593, July 31st, 1923, 227.143, August 3rd, 1923, 228.814, August 3rd, 1923, 247.296, July 12th, 1922. Blumenfeld, British Patents 253.550, June 11th 1925, 275.672, August 9th, 1927, 310.949, May 5th, 1928, 360.436, August 2nd, 1930, 385.315, December 19th, 1932.
9. Tillmann, German Patent 700.918, April 1937.
10. M. Toch, Paints, Painting and Restoration, (New York: D. Van Nostrand Co, 1931), 105.
11. A. Eibner, Malmaterialienkunde als Grundlage der Maltechnik für kunststudierende Künstler, Maler, Lackierer, Fabrikanten und Händler, (Berlin: Julius Springer, 1909), 143-144.
12. R. Mayer, The Artists' Handbook of Materials and Techniques, (New York: The Viking Press, 1970), 5.
13. J. Fiedler, M.C. Bayard, Artists' Pigments, a handbook of their history and characteristics, Cadmium Yellows, Oranges and Reds, vol 1, (Cambridge: University Press, 1986), 80-81.
14. H. Kittel, Pigmente, Herstellung, Eigenschaften, Anwendung, (Stuttgart: Wissenschaftliche Verlagsgesellschaft, 1960), 200-201.
15. K. Heinle, "Die Pigmententwicklung seit 1947", Deutsche Farben-Zeitung, 21, no 8 (1967), 401.
16. E.L. Moore, Pigment Handbook, Cadmium/Mercury Sulfides, vol 1, (New York: John Wiley & Sons, 1973), 396-397.
17. H.W.D. Ward, "New Cadmium Pigments", The Chemical Trade Journal and Chemical Engineer, 80, (1927), 59-60.
18. R.J. Gettens, G.L. Stout, Painting Materials, a short encyclopaedia, (New York: Dover Publications, 1966), 102.
19. Kittel, "Pigmente", 197-198.
20. Lederle, German Patent no 22 F. 1.52.30, August 30th, 1930, I.G. Farbenindustrie A.G.
21. Lederle and Grimm, German Patents 574.379, 12.4.1933, 574.380, 13.4.1933, U.S. Patent 1.926.447, 12.9.1933, Yellow to Red Pigments.
22. Kittel, "Pigmente", 288-289.
23. Heinle, "Die Pigmententwicklung seit 1947", 400.
24. Gettens, "Painting Materials", 128.
25. K. Wehlte, Werkstoffe und Techniken der Malerei, (Ravensberg

Otto Maier, 1967), 120-121.

26. M. de Keijzer, "Zaans Molenpanorama van Frans Mars (1903-1975) in het Molenmuseum te Koog-Zaandijk", I.I.C. Mededelingenblad, 6, no 3, (1989), 22-27.
27. M. Fischer, The permanent palette, (New York City: National Publishing Society, 1930), 29.
28. C. Couprie, J. le Marec, J. Corset, M.C. Papillon, R. Lefèvre, A. Duval, C.H. Lahanier, J.P. Rioux, "Analyses de Pigments Blancs Appliquées à l'Etude Chronologique des Peintures de Chevalet - Blanc de Titane", Preprints, 8th Triennial Meeting, ICOM - Committee for Conservation, Sydney, Australia, (1987), 25-32.
29. M. de Keijzer, "The Preparation and the Examination of Paint Cross-Sections, Applied to Paintings by Vilmos Huszár", The Fifth International Restorer Seminar, Veszprém, Hungary, (1985), 127-135.
30. Fischer, "The permanent palette", 98.
31. R. Mayer, A Dictionary of Art Terms and Techniques, (New York: Thomas J. Crowell, 1969), 288.
32. F. Kerdijk, Kunstschildersmaterialen en schildertechniek, (Apeldoorn: Talens en Zoon N.V., 1937), 20, 45.

ABSTRACT

This paper presents a survey of the history and development of the blue, green, violet, orange and brown synthetic organic artists' pigments discovered, produced and used in the 20th century. The following organics are described: copper phthalocyanine blue, metal-free phthalocyanine blue, indanthone blue, phthalocyanine green, pigment green B, nickel-azo-yellow, quinacridone violet, dioxazine purple, dinitraniline orange, perinone orange and PV Fast Brown HFR.

The chemical identification can be done by micro-chemical colour-reactions, micro-crystallizations, laser-microspectral analysis and infrared spectrophotometry. These methods of analysis together with the discovery dates of the individual pigments enable dating modern works of art (a date "post-quem") and detection of forgeries.

KEYWORDS

Artists' pigments, synthetic organic, twentieth century, history, micro-chemical analysis, colour reactions, micro-crystallizations.

MICROCHEMICAL ANALYSIS ON SYNTHETIC ORGANIC ARTISTS' PIGMENTS DISCOVERED IN THE TWENTIETH CENTURY

Matthijs de Keijzer
Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 8
1071 EA Amsterdam, The Netherlands

Introduction

The pigment lists of manufacturers show that 50 to 70% of the artists' pigments used today, were discovered in the twentieth century. The discovery of copper phthalocyanine blue was a turning point in pigment chemistry and a start for the "all-round" and "high-grade" pigments. Pigment chemists tried to produce pigments of equal fastness, but in varying shades, by subjecting this molecule to every substitution and variation. This led to products exhibiting lower fastness and/or less attractive shades, with one exception: phthalocyanine green. Therefore the pigment chemists investigated other chemical classes for pigments which have the high standard of the phthalocyanines, but in other shades. After the end of World War II considerable progress was made both in improving existing high quality pigments and in developing new pigments, and specifically pigments prepared from textile colorants known as vat colours.

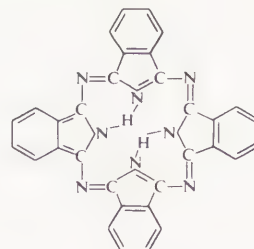
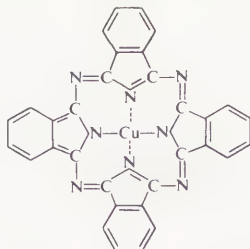
The author has hope that this method of identification will lead to finding of organic coloured pigments in well-dated objects made shortly after the introduction of these pigments.

History and development

Because in the literature no book has been found in which the relation between the industrial development and the history of the introduction of modern artists' pigments on the one hand and the paint technical properties on the other hand thorough investigation into literature and patents has been done in order to establish not only the chemical history but also the chronology of the pigments.

Copper phthalocyanine blue, PB 15, (74160), $C_{32}H_{16}N_8Cu$

Metal-free phthalocyanine blue, PB 16, (74100), $C_{32}H_{18}N_8$

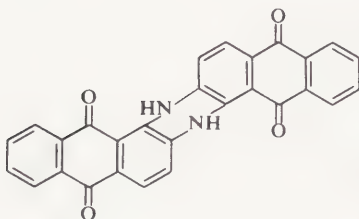


In 1907, Braun and Tscherniak, working at the South Metropolitan Gas Company in London, found a trace of a blue substance. In 1927 De Diesbach and Von der Weid heated o-dibromobenzene and cuprous cyanide in pyridine at 200°C,

attempting to obtain phthalonitrile, but instead they got a deep blue product containing copper, their product undoubtedly was copper phthalocyanine. They observed the remarkable stability to alkalis, concentrated sulphuric acid, and heat. A year later, independently, chemists (Dandridge, Drescher and Thomas) at the Grangemouth works of Scottish Dyes Ltd observed coloured compounds produced in an open vessel by reaction of ammonia with molten phthalic anhydride, phthalamide or phthalimide in the presence of metals. In 1929 the first patents were issued by these chemists (British Patent 322.169 and German Patent 586.906). Up to 1929, none of the observers attempted to determine its structure. British chemists saw the commercial possibilities in such pigments and Professor Reginald P. Linstead at the Imperial Institute of Science and Technology of London, supported by grants from Imperial Chemical Industries Ltd during 1933/34, elucidated the structure and synthetic pathway of the important group now known as phthalocyanines. The structure of phthalocyanine was published in 1934 and therefore the year of discovery of the phthalocyanine class of organic compounds is said to be 1934. In 1932 I.C.I. patented the manufacture of phthalocyanines (U.S. Patents 2.000.051 and 2.000.052, 1932) followed by the British Patents 410.814 (1934), 464.126 (1935) and 476.243 (1936). The pigment industry then attempted the manufacture of phthalocyanines. The first pigments appeared in 1935 by the Imperial Chemical Industries Ltd under the trade name Monastral Fast Blue B.S. As an industrial pigment phthalocyanine blue was first showed in 1935 on an exhibition of

I.C.I. in London. In 1934 research in Germany, Ludwigshafen and Leverkusen, led to patents (German Patents 658.019 (1934) 663.552 (1935), I.G. Farbenindustrie A.G.). One year later (1936) I.G. Farbenindustrie A.G. followed in Germany at Ludwigshafen under the trade name Heliogenblau B Pulver (BASF A.G.). In the same year E.I. du Pont de Nemours & Company started to produce this blue pigment at Deepwater Point, New Jersey, United States (U.S. Patents 2.173.699 (1936) and 2.247.752 (1937)). Since the development of the first phthalocyanine blue, there have been many improvements. A high point is the β -modification of phthalocyanine blue. Phthalocyanine blue metal-free was discovered by Thorpe, Linstead and Thomas in 1931 (Scottish Dyes Ltd, British Patent 389.842) and was available through the period 1945 to 1955. It was replaced by β -copper phthalocyanine blue and its manufacture was discontinued.

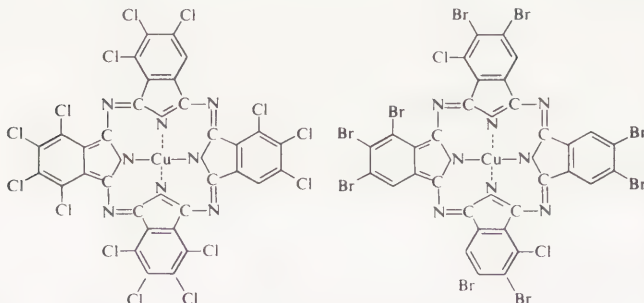
Indanthrone blue, PB 60, (69800), $C_{28}H_{14}N_2O_4$



During the period of investigation of indigo derivatives in 1901, René Bohn attempted to prepare an anthraquinone derivative of indigo; he got a blue compound named as indanthrene (indigo of anthracene). It is now generally known as indanthrone. In 1924 German companies were amalgamated into the I.G. Farbenindustrie A.G. and Bohn's original name Indanthrene was applied as trade name by the constituent firms.

Phthalocyanine green, PG 7, (74260), $C_{32}H_0N_8Cl_{14}Cu$

Phthalocyanine green, PG 36, (74265), $C_{32}H_4N_8Br_{12}Cl_4Cu$

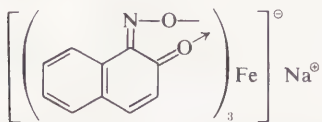


In August 1935, soon after the determination of the structure of phthalocyanine, Linstead and Dent discovered phthalocyanine green, while Niemann, Schmidt, Mühlbauer and Wiest did the same in December of that year.

Phthalocyanine green

is obtained by direct chlorination of copper phthalocyanine suspended in molten phthalic anhydride or sodium aluminium chloride. I.C.I. Ltd started in 1936 with the production under the trade name Monastral Fast Green GS, followed two years later by I.G. Farbenindustrie A.G. under the trade name Heliogen Grün B and in 1940 by Du Pont, United States. The development of phthalocyanine green received a boost when Harmon Colors discovered chlorobromocopper phthalocyanine in 1957 and the shade becomes yellower with increasing bromine content. These yellow-green phthalocyanines (PG 36, 74265) came into use in America in 1959.

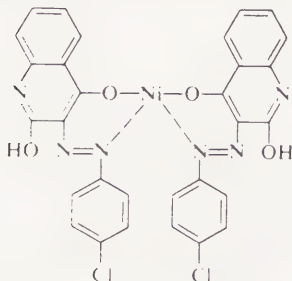
Pigment green B, PG 8, (10006), $C_{30}H_{18}N_3O_6FeNa$



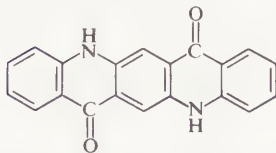
With the exception of alizarine lake, pigment green B is the oldest chelate pigment of commercial significance. It was first reported in 1885 by Hoffmann.

Since he foresaw no possibility for its technical utilization he did not apply for a patent to cover its manufacture. In 1921 BASF A.G. developed a procedure which yielded the compound in a form suitable for pigment use (German Patent 356.973). It reached a peak in the early 1950's before phthalocyanine green began to make inroads into its markets.

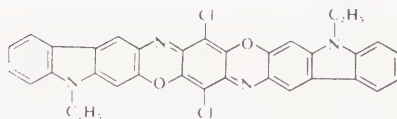
Nickel-azo-yellow, PG 10, (12775), $C_{30}H_{18}O_4N_6Cl_2Ni$



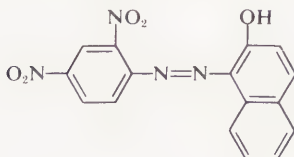
After the World War II nickel-azo-yellow was developed by Woodward and Kvalnes, working by E.I. du Pont de Nemours & Company. It is covered by the U.S. Patents 2.396.327 and 2.396.328 (March 12th, 1946) and it was introduced to the trade by Du Pont under the name YT-562-D Green-Gold in 1947.

Quinacridone violet, PV 19, (46500), $C_{20}H_{12}N_2O_2$ 

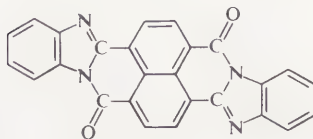
The name quinacridone was coined by Niementowski in 1896. Ten years later Ullmann and Maag obtained a product with yellow needles m.p. 394°C, to which they ascribed to linear structure of quinacridone. The first example of the synthesis of the basic linear quinacridone ring system was quinacridonequinone prepared by Sharvin in 1915. The preparation of the first linear-cis-quinacridone was described by Eckert and Seidel in 1921. The linear-trans-quinacridone system remained unknown until 1926 when Lesnianski and Czerski were the first persons to synthesize it. A procedure for the preparation of another class of compounds in this series, the dihydroquinacridones, was claimed by Pendse and Dutt in 1932. Unsubstituted linear-trans-quinacridone, a red-violet powder, was first synthesized by Liebermann in 1935. The quinacridones attracted particular attention until 1955, when chemists in the Pigment Department of E.I. du Pont de Nemours & Company discovered its excellent lightfastness and methods for the preparation of its different crystal forms. Quinacridone can exist in four different crystal forms (α , β , γ and δ -modifications). Only two provided commercially important pigments (the violet and the bluish-red forms). The differences in the X-ray patterns are mentioned in the U.S. Patent 2.844.485 by Struve in 1959. The first quinacridone pigments were introduced by E.I. du Pont de Nemours & Company in 1958 under the registered trade name Monastral. Three colours were available: Monastral Red B, Monastral Red Y and Monastral Violet R. Hoechst A.G. was the first company in Europe which produced linear-trans-quinacridone soon after E.I. du Pont de Nemours & Company produced it in the United States. Struve described in the U.S. Patent 2.821.529 (January 28th, 1958) and complementary patents method to produce linear-trans-quinacridone. A variety of syntheses for quinacridones appears in the scientific and patent literature and is covered in the article "Quinacridones" by Labana and Labana. By virtue of continued research by the pigment industry the spectrum of the quinacridone pigments has been expanded and they are marketed since the late 1960 in colours ranging from oranges to golds, reds, maroons to magentas and violets.

Dioxazine purple, PV 23, (51319), $C_{34}H_{22}N_4O_2Cl_2$ 

The most important carbazole dioxazine pigment today is dioxazine purple. It was probably discovered by Kranzlein Gruene and Thiele in the late 1920' (1928, Farbwerke Hoechst) when they were exploring the chemistry of oxazine dyes. It is mentioned as a dyestuff and pigment in the U.S. Patent 2.016.013 issued to General Aniline and Film Corporation on October 1, 1935. In 1952 Hoechst A.G. found that by special conditioning processes a good dioxazine pigment was obtained (German Patent 946.560, 1952) and one year later it was introduced as Permanentviolett RL (today Hostaperm Violet RL). In 1958 E.I. du Pont de Nemours & Company started to produce dioxazine pigments (U.S. Patent 2.857.400, Cooper, 1958).

Dinitraniline orange, PO 5, (12075), $C_{16}H_{10}N_4O_5$ 

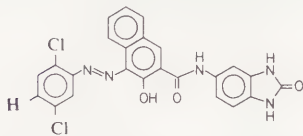
Dinitraniline orange is based on the diazo-reaction that was discovered by Griess in 1859. A year later he prepared the first azo dyestuff called amidazo benzene and in 1863 it was manufactured commercially under the name Anilin Yellow by Simpson, Maule and Nicholson. Dinitraniline orange was discovered in 1907 by R. Lauch and in 1909 the preparation of it (Permato Orange) was disclosed in the German Patent 217.266 and U.S. Patent 912.138 by A.G.F.A..

Perinone Orange, PO 43, (71105), $C_{26}H_{12}N_4O_2$ 

The perinone group has one orange and one red pigment, discovered by W. Ecker and H. Greune (Farbwerke Hoechst) in 1924 as a mixture of isomers. The trans form of perinone orange, is by far the more important of the two perinone pigments. In the beginning of

the fifties one was able to separate the isomers and the use of perinone orange as a pigment started after 1950. The pigment was produced by Hoechst A.G. as Hostapermorange GR (formerly Indanthrenbrillantorange GR). Heinle is more detailed about the year that Hoechst A.G. put Indanthrenbrillantorange GR on the pigment market, 1953.

PV Fast Brown HFR, PBr 25, (12510), $C_{24}H_{15}N_5O_3Cl_2$



The first patent for the benzimidazolone pigments was applied in 1960 by Farbwerke Hoechst, U.S. Patent 3.124.565. The next patents described different processes to manufacture benzimidazolones: Germans Patents 1.213.552 and 1.215.839, U.S. Patents 3.109.842 and 3.137.686 and the Belgian Patents 723.711 and 723.012, all patented by Hoechst A.G. The benzimidazolones made their first appearance in West-Germany in 1964. PV Fast Brown HFR was introduced in Europe in the Hostaperm range in December 1966.

The use as an artists' pigment

When artists started to use the synthetic organics as artists' pigments is not known exactly. In the first half of this century the artists were taught to limit their palettes strictly to the permanent inorganic pigments plus alizarine crimson. As recently as 1950 alizarine crimson, phthalocyanine blue and phthalocyanine green were the only three synthetic organic pigments universally approved for use by artists. It has been assumed that an accurate date "post-quem" for art-objects is the year of discovery or the first production of the new pigment. In practice, one must consider that a new pigment is not used directly as an artist's pigment. On the contrary, it is the last link in the chain. It is noted that only a few investigations of modern well-dated works of art have been performed.

Nickel-azo-yellow is the most lightfast azo-pigment known to commerce. Its excellent lightfastness combines good alkali, acid, and heat resistance. Its greenish hue makes it useful in a variety of applications. Green-Gold YT-526-D has a green colour masstone, but it is a greenish-yellow in tint tone. It is transparent, therefore it has low to medium hiding power, but it is strong in tints. Its greenish tone makes it suitable for blending with phthalocyanine blues and greens to produce permanent and brilliant greens. Pigment green B is a pigment produced exclusively for specific applications, such as wallpaper, and of hardly any importance. This pigment possesses a semitransparent masstone, dull yellowish tint, and excellent alkali resistance. Its value for these applications is its good alkali resistance and economy in cost but is too sensitive to acids. In paints, it is sometimes used in preference to chrome green, because of its superior alkali resistance and it is favoured over chromiumoxide because of its brighter colour and lower cost. It may also be favoured, over phthalocyanine green because of its economy. It is not used in masstone, because it is almost greenish black in colour.

Carbazole dioxazine violet has outstanding tinctorial strength, brightness, excellent heat and bleed resistance and good lightfastness. These superior qualities tend to offset its relatively high cost. It is used as a violet pigment and for producing reddish-blue shades in combination with phthalocyanine blue. In artists' pigments it is mostly mixed with quinacridone red (PR 122), titanium dioxide (PW 6) and phthalocyanine blue (PB 15).

Quinacridone violet combines outstanding tinctorial properties with heat and chemical resistance, lightfastness and non-bleeding properties. It is of considerable interest, because of its masstone depth, transparency as well as tint intensity.

Indanthrone blue is hardly used as an artist's paint because, in comparison with phthalocyanine blue, it is more expensive. It shows no tendency to crystal growth and is flocculation resistant. Although generally good in bleed and chemical resistance it is susceptible to reduction, and tints may show a slight tendency to bleed and give a change in colour and so to non-permanence of the painted surface. These two limits make it not suitable for use as an artist's pigment.

The best organic green pigment is phthalocyanine green. It possesses a clean tint, high strength, a semitransparent masstone, excellent resistance, to heat, chemicals and is non-bleeding. It is lightfast in both masstone and tint, but is dark in mass tone and, thus rarely used and shows a tendency to bronze on exterior exposure. Phthalocyanine green is stable and is available in shades ranging from a bluish green to a yellowish green. As an artist's

pigment it was already produced by Messrs Winsor & Newton in 1933 and Royal Talens put it on their pigment list in 1940. The most important organic blue pigment is phthalocyanine blue. It possesses a semitransparent masstone, high tinting strength and has a clean hue. It is non-bleeding and has an excellent resistance to heat and chemicals. In comparison with Prussian blue it has a better tinting strength, a cleaner hue and enjoys good resistance to alkaline media. These are the reasons why Prussian blue largely disappeared from the artist's palette and phthalocyanine entered it rapidly. One can say that phthalocyanine blue is the modern, reliable replacement for Prussian blue. Ground in oil it absorbs much. The blue pigment is generally found amongst the cheaper artist's oil colours. Soon after its discovery Messrs Winsor & Newton started to produce it in 1937 as an artist's pigment. Royal Talens mentioned it first in 1940 under the name Rembrandtblauw. In the painting "Who's afraid of red, yellow and blue III," (1967) by Barnett Newman, phthalocyanine blue is analysed. Perinone orange possesses a clean yellowish shade and good fastness to light, heat and solvents and therefore widely used. Up to now it is the most expensive pigment, 80 to 90 pounds for one kilogram, because one has to separate the cis and trans form. Dinitraniline orange has very good overall pigment properties, a clean colour, good lightfastness and a reasonable price. The advantage in comparison with minium and chrome orange is that it does not darken. In every respect with perinone orange all pigment properties are lesser. PV Fast Brown HFR possesses a redbrown colour, good lightfastness, alkali, acid, and heat resistance. Royal Talens uses it in combination with alizarine crimson (PR 83) and as a pure product.

The chemical identification

The modern pigments are finely ground in comparison with the classical pigments (smaller than one micron). Pigment characteristics in the paint layers in a paint cross-section under a microscope with a magnification up to 1000 times cannot be observed and recognized well. Besides microscopic investigation analytical methods are used to identify the pigments in a paint sample. In case of doubt or if one is in the need of an indisputable chemical analysis one has to choose the method which gives a satisfying answer. The method of choice varies. The organics can be investigated by colour-reactions, making good use of the paint cross-section. The identification is based on reactions with concentrated sulphuric acid. The characteristic colour changes generally serve as an excellent means of identification. Concentrated nitric acid and concentrated alcoholic potassium hydroxide are also used to produce different colour reactions. These reactions reliably identify pigments and offer the advantage of being applied to paint cross-sections without the need for separation of the layers. In practice the paint layers contain mixtures of pigments rather than single pigments. The coloured pigments are normally mixed with white pigments, such as the titanium dioxides, zinc white or barium sulphate. Luckily; these white pigments are inert and do not interfere. As organic pigments are found in many varied concentrations it is necessary to evaluate approximately the sensitivity of the chemical tests. For this a series of mixtures is made up from a white pigment (titanium dioxide, rutile-modification) and various concentrations of phthalocyanine blue. The results showed that the pigments could be identified to an approximate concentration of 30% coloured organic pigment in 70% titanium dioxide. In tube paint the concentration of the coloured organic pigment usually is higher than this detection limit. Reactions obtained below this concentration were weak and difficult to observe. This result indicates that these chemical tests can be used only to identify the major single coloured pigments in paint cross-sections. A mixture of two or more tinter pigments in a paint layer offers a problem. Generally only one major pigment can be detected by these chemical tests.

After the colour-reactions the fresh polished surface of the paint cross-section can be used for laser-microspectral analysis. This is a simultaneous multi-element method. The result of this spectrographic analysis is a series of elements with a rough indication of the relative concentration of each element. One can establish whether the pigments used are pure or have been mixed. The inorganic pigments especially can be determined so one can analyse with which inorganic pigments the organic is mixed or which metal chelate a pigment contains.

Some modern synthetic organic pigments can also be identified by micro-crystallizations, such as copper phthalocyanine blue, metal-free phthalocyanine blue, nickel-azo-yellow and dinitraniline

orange. Prepared loose powdered pigment from a paint sample is placed on a microscope glass. After placing a cover slip over the dry paint, it is rubbed until the powder is spread uniformly. A small drop of concentrated sulphuric acid is dropped on the extreme edge of the cover slip and through capillarity action the liquid quickly spreads. By examining a field near the edges crystal growth will soon be observed. The micro-crystallizations are specific to these organics. Infrared spectrophotometry is also helpful to identify the synthetic organic pigments. The disadvantage of the last two methods is that one cannot use the paint cross-section, a separate small paint sample is required.

Table 1. Colour reactions of the synthetic organic artists' pigments

Pigments	Reagents and reactions		
	concentrated sulphuric acid	concentrated nitric acid	concentrated alcoholic potassium
Copper phthalocyanine blue, PB 15 and phthalocyanine blue metal-free, PB 16	solid turns green yellow, t=0' then dissolves to a colourless solution, t=3' to 15'	solid turns purple, t=0' or green then purple, t=3'	no change
Indanthrone blue, PB 60	solid turns orange brown t=0' to 3' then dissolves to colourless solution, t=3'	solid turns green yellow t=0' to 3'	no change
Quinacridone violet, PV 19	dissolves to give mauve, then colourless solution, t=3'	solid becomes purple, t=0'	blue colour emitted from edges t=0', then flake blue, t=3'
Carbazole dioxazine violet, PV 23	blue colour emitted from edges, t=0', then dissolves to blue/green solution, t=15'	solid dark green, t=0'	no change
Phthalocyanine green, PG 7	solid turns yellow, t=0' to 3'	no change	no change
Pigment green B, PG 8	dissolves to give brown brown solution, t=0' to 3'	solid turns yellow green, t=0' colourless, t=3' to 15'	no change
Nickel-azoyellow, PG 10	dissolves to give orange/brown solution, t=3'	partly dissolves to give yellow solution, t=3'	no change
Dinitraniline orange, PO 5	solids turns purple, t=0'	no change	blue colour, t=0', then green yellow colour, t=3'
Perinone orange, PO 43	yellow red colour, t=0'	solid turns yellow, t=0'	reddish brown colour, t=0'
PV Fast Brown HFR, PBr 25	solid turns purple, purple, t=0'	no change	no change

Bibliography

- F.H. Moser, A.L. Thomas, Phthalocyanine Compounds, ACS Monograph 157, (New York: Reinhold Publishing Corporation, 1963).
- T.C. Patton, Pigment Handbook, Vol 1, (New York: John Wiley & Sons, 1973).
- S.S. Labana, L.L. Labana, "Quinacridones", Chemical Reviews, Volume 67, no 1, (1967).
- W. Herbst, K. Hunger, Industrielle Organische Pigmente, (Weinheim: VCH Verlagsgesellschaft GmbH, 1987).
- K. Heinle, "Die Pigmententwicklung seit 1947", Deutsche Farben-Zeitung, 21, no 8 (1967).
- L.S. Pratt, The Chemistry and Physics of Organic Pigments, (New York: John Wiley & Sons Inc, 1947).



Working Group 7

Wet Organic Archaeological Materials

Matériaux organiques archéologiques

gorgés d'eau



ABSTRACT

A waterlogged wooden "Oberländer", a medieval river craft from the Rhine was salvaged in 1973. It was built of very wide and up to 12 cm thick boards of European oak, and the individual boards comprised wood in different states of degradation. So a two-step polyethylene glycol (PEG) treatment was applied for the dimensional stabilization of the timbers using 43 % PEG 200 and 70 % PEG 3000. Progress of the impregnation was monitored by HPLC of extracts gained from segmented fine wood cores taken at time intervals with an increment borer. Total stabilization was achieved, but the PEG-analysis showed the necessity to insert an extraction step between the two PEG impregnations to increase the hardness of the surface.

KEYWORDS

Waterlogged wood
PEG two-step treatment
PEG-analysis
High performance liquid chromatography (HPLC)

A WATERLOGGED MEDIEVAL RIVER CRAFT FROM THE RHINE STABILIZED IN A TWO-STEP POLYETHYLENE GLYCOL TREATMENT

Per Hoffmann
Deutsches Schifffahrtsmuseum
2850 Bremerhaven
Federal Republic of Germany

Introduction

In January 1973 amateur divers aided by a lorry and steel wires dragged a medieval river craft from the ice-clad muds of an old backwater of the river Rhine near Krefeld, plank by plank. The 6-meter-ship turned out to be a small so-called "Oberländer", dated to the 13th - 14th century by pot-sherds found in it (fig. 1). It came to the German Maritime Museum which was just being established at that time. Here it had to wait another 10 years sitting in a waterfilled polyethylene film lined wooden tank until appropriate conservation facilities could be constructed - a workshop for large objects with two heatable impregnation tanks of 5 meters interior length.

Dimensional stabilization of waterlogged wood with PEG has been practised since the early 1950s, mostly using PEG 4000 or PEG 1500. Grattan and Clarke give a comprehensive historical review (1). In the early eighties, however, research intensified into the question what molecular size PEG could really enter into archaeological wood of different species and states of degradation (2-6). It turned out, and became generally accepted, that no one PEG can stabilize all wood qualities to an acceptable extent. Low molecular weight PEG or high molecular weight PEG have to be chosen for little degraded or highly degraded wood respectively.

Development of a two-step treatment

Waterlogged archaeological timbers exceeding a few centimeters in thickness usually contain wood of several distinct qualities. An outer layer of heavily degraded tissue envelops an inner core of less degraded wood. A narrow transition zone may be present between these two areas. This pattern is particularly typical of European oak, but it is also found in most other species. In the early eighties the center-piece of the German Maritime Museum, the 'Bremen Cog', a 23-meter medieval seagoing merchantman, was ready for conservation. Its 30 tons of multi-quality oak-timbers could not be expected to be stabilized satisfactorily with one PEG alone. So test series were carried out in order to establish an appropriate conservation schedule (7).

PEG with molecular weights from 200 to 3000 were tried on



fig. 1: The medieval "Oberländer" from Krefeld/Rhine in 1973 arranged from its individually salvaged planks. Length 6 m, width 1.7 m.

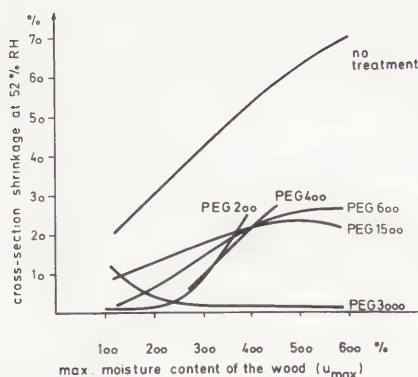


fig. 2: Stabilizing effect of various polyethylene glycols (PEG) on oakwood of different degrees of degradation (expressed as maximum moisture content). Concentration of the treatment solutions: 30 % for PEG 200, 400, and 600; 80 % for PEG 1500 and 3000. Data from (5) and (7).

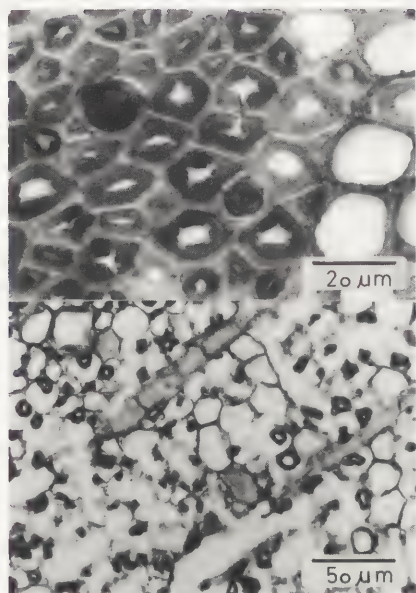


fig. 3: Waterlogged oakwood, light microphotos.

TOP: slightly degraded wood with swollen cell walls (cell walls in fiber cells bulge into the cell lumina). Bottom: heavily degraded wood. Secondary cell walls partly completely degraded and absent, partly present only in degenerated and shrunken form (dark "rings" within the system of remaining middle lamellae).

wood of different states of degradation the maximum water content (u_{\max}) of which ranged from 120 % (sound wood) to 580 % (heavily degraded wood). The residual shrinkage of the test specimens after air-drying is shown in fig. 2. Several interesting results can be seen. Low molecular weight PEG (200 and 400) stabilized little degraded wood ($u_{\max} < 250$ %) very well, high molecular weight PEG 3000 stabilized heavily degraded wood ($u_{\max} > 250$ %) very satisfactorily. The PEGs with medium molecular weight (600 and 1500) did not work very well on any wood quality. The most pleasant result was that evidently the whole range of wood qualities can be stabilized with only two PEGs, eg. PEG 200 and PEG 3000. Where the efficiency of one PEG stops the efficiency of the other starts.

The obvious conclusion is to use a low and a high molecular weight PEG on multi-quality timbers. The simple way to impregnate the wood in a mixture of PEGs has one prohibiting drawback. Such a mixture will not become hard on drying, but stay pasty, sticky and hygroscopic. It would impart these unacceptable characteristics to the wood thus treated. Instead, the two PEGs have to be applied one after the other in separate impregnation baths.

The underlying idea of such a two-step treatment is as follows. During the impregnation with a low molecular weight PEG, eg. PEG 200, this PEG penetrates through the highly degraded and quite permeable outer parts of the timbers (fig. 3) and into the little degraded inner parts. Here it not only occupies the cell lumina but also diffuses into the capillaries of the cell walls where it replaces part of the water which has brought the cell walls into a swollen state (fig. 3). Hydrogen bonds form between the PEG-molecules and the compounds of the wood substance.

In the second treatment, with a solution of high molecular weight PEG, eg. PEG 3000, this PEG diffuses only into the better penetrable decayed wood tissues. Here it fills the cell lumina and the residues of cell walls to a high degree. At the same time PEG 200 which is not trapped or bound in the cell walls of the lesser degraded wood diffuses out again of the timbers.

So, at the end of the treatment there should be PEG 200 in the cell walls where such are present, mainly in the lesser degraded wood, and PEG 3000 in the cell lumina and wide pores of heavily degraded cell walls in the strongly decayed wood. On cooling and drying of the wood the liquid PEG 200 keeps the infiltrated cell walls in their swollen state, and the PEG 3000 solidifies to a hard, dry state bulking the remnants of the degraded tissue against shrinkage and collapse. No PEG-mixture should form in the surface layers of the wood, and so the bad effects of such a mixture are avoided.

Treatment of the "Oberländer"

In 1984 a first tank was filled with the boards of the "Oberländer" and some other items, and treatment started along the outlined idea. The concentration of PEG 200 was gradually raised from 18 to 43 % during 20 months, the temperature of the solution being kept at 40°C to enhance the diffusion of PEG into the wood.

To monitor the progress of a two-step treatment it is necessary to quantitatively determine different PEGs simultaneously in a wood sample. Such a method had to be developed. Unfortunately it took longer than expected to develop a high-performance liquid-chromatographic HPLC separation and determination technique for PEGs of a wide range of molecular weights (8,9) and to raise money for the necessary equipment. Therefore, the "Oberländer" had to stay another year in the 43 % PEG 200 bath until the degree of PEG-penetration could be checked.

A core sample 5 millimeters in diameter was taken through the thickest plank (12 cm), and divided into segments 10 - 20 mm long. The segments were finely cut to shavings, extracted with a minimum of water, and the filtered extracts HPLC-analysed for PEG. The analysis showed that the diffusion of PEG had come to equilibrium, the water in the wood had throughout the board acquired the PEG-concentration of the treatment solution in the bath (fig. 4, left, lower graph). The analysis of a core through a 13 cm thick rib gave the same result.

The treatment solution was then exchanged for a 45 % PEG 3000 solution, and the temperature raised to 60°C. Within 10 months the PEG-concentration was raised in three steps to 70 %, and then the bath was kept at that for another 4 months. Core samples were taken after 2 and 11 months. Their analyses are given in fig. 4.

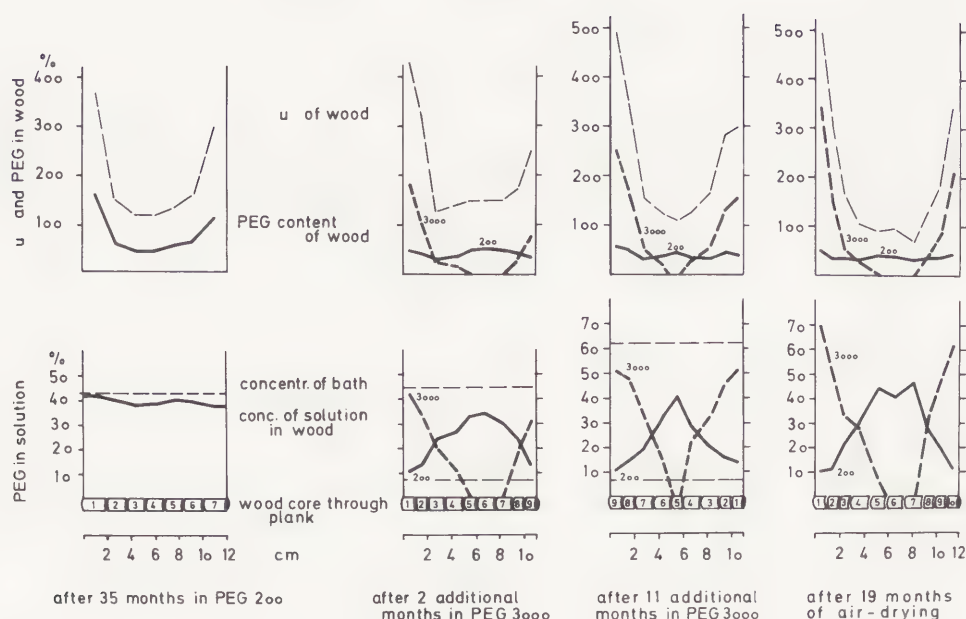


fig. 4: Analyses of core samples taken during the conservation treatment of the "Oberländer", and after 19 months of air-drying. Maximum moisture contents (u_{max}) could not be determined, so only the actual moisture content (u) is given which may be up to 10 % lower than the respective u_{max} .

Actually, in treated wood the value determined for u comprises water and the PEG that has substituted part of the original water.

After two months in the second bath the concentration of PEG 3000 in the water in the wood (lower graph) has reached a high level in the outermost parts of the plank, but decreases rapidly towards the inner parts. In the core of the plank no PEG 3000 can be detected. At the same time the concentration of PEG 200 has decreased considerably in the water in the outer parts of the plank, as expected.

Nine months later, the treatment solution being at 62 % PEG 3000, the diffusion processes have advanced. More PEG 3000 has entered the wood and has penetrated deeper into it. But still the innermost parts of the plank contain minimal to no PEG 3000. At the same time more PEG 200 has left the outer parts of the plank. However, even in the outermost layers the water in the wood still contains 10 - 14 % PEG 200.

The reason for this was found in the analysis of the bath solution, which contained 7 % PEG 200. This was the PEG 200 leached out of the wood, and the amount was larger than anticipated.

After 4 months at 70 % PEG 3000 the treatment solution was pumped off the tank, and the timbers were cleaned from adherent solution with soft brushes and very little hot water. On cooling to room temperature the treatment solution in the wood set to a hard but not brittle consistency, due to its content of PEG 200.

At relative humidities (RH) below about 70 % the surface of the timbers are dry, but at higher RH they become soft, wax-like, and a bit sticky. This is not so dangerous as the "Oberländer" will be exhibited in a modern, climate-controlled museum. But it demonstrates the necessity on principle to avoid any mixture of high molecular weight PEG with even small amounts of low molecular weight PEG. So, in future treatment cycles a washing step will have to be inserted after the PEG 200-step, and tests will have to show how long such a washing must and can last to extract the PEG 200 from only the outer wood layers.

The stabilization effect of PEG 200 and PEG 3000 depends on the amount of PEG incorporated into the wood. From the laboratory test series mentioned earlier emerged two simple relations for the best dimensional stabilization of oakwood, which correlate the necessary amount of PEG to the state of degradation of the wood



fig. 5: A model of the original "Oberländer"

expressed as its maximum water content (u_{\max}):

$\text{PEG } 200_{\text{optimal}} = 0,5 u_{\max} - 15$ for slightly degraded wood,

$\text{PEG } 3000_{\text{optimal}} = 0,66 u_{\max}$ for heavily degraded wood,

where $\text{PEG}_{\text{optimal}}$ and u_{\max} are given in percent based on dry wood substance.

These equations are empirically derived for waterlogged oak-wood. A set of two similar equations, but with lower numerical values, have been found for 4 softwoods (10). It remains to be investigated if the equations for oakwood should also be valid for other deciduous (broad-leaved) species.

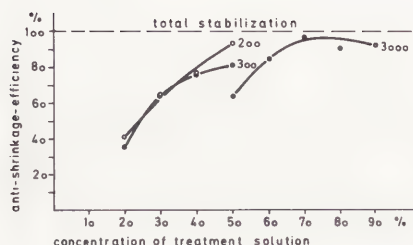


fig. 6: Anti shrinkage efficiency (ASE) of PEG-solutions of various strength on slightly degraded oakwood ($u_{\max} = 168\%$) for PEG 200 and 300, and on heavily degraded oakwood ($u_{\max} = 385\%$) for PEG 3000. ASE describes to what extent a treatment suppressed the shrinkage on drying that would occur in a non-treated wood sample. ASE = 100 % means that shrinkage has been totally suppressed.

$$\text{ASE} (\%) = \frac{\beta_0 - \beta_i}{\beta_0} \times 100$$

β_0 = shrinkage untreated wood

β_i = shrinkage treated wood

The optimal amounts of PEG are introduced into oakwood when the treatment solutions have a concentration of 50 % for PEG 200, and 70 % for PEG 3000, and when the water in the wood has come to equilibrium with the respective solutions. A warning, however, must be expressed here. Oakwood impregnated with a 50 % PEG 200 solution contains much more PEG than can be bound in the cell walls. Why a surplus of liquid PEG 200 in the cell lumina enhances the stabilization I cannot say. But with time PEG will seep out of the wood, make it feel moist and sticky, and produce grease-spots on its support. So we only use PEG solutions up to about 35 % in treatments with PEG 200 only. In two-step treatments, where the surplus PEG has time to diffuse out again, higher concentrations are useful to keep the diffusion going. For the first step on the "Oberländer" a final concentration of 43 % PEG 200 (45 % were intended) was chosen. The end concentration of the second treatment step - 70 % PEG 3000 - represented the optimal value found in the lab tests (fig. 6).

The graphs in the upper row of fig. 4 not only give a picture of the degradation profile across the analysed board - expressed by the curves for u -, but by giving the contents of PEG based on wood substance they also make it possible to check to which degree the ideal PEG-uptake has been achieved.

After 19 months of air drying a last analysis was made of the wood (fig. 4, right). The determination of the content of solution (PEG + H_2O) across the plank, expressed as " u " in the upper graph showed that next to no water seems to have evaporated from the wood. The values for u are in the same magnitudes as those from the cores taken during the immersion of the plank. Due to the physical bulking of the surface layers of the wood with PEG, and to the water retention ability of the PEG, it will probably take many years for the treated wood to come to the equilibrium which can be foreseen from the hygroscopicity characteristics of wood and of PEG. And only in years can we decide about a final surface treatment for the ship.



fig. 7: Large "Oberländer" ships on the Rhine, on a prospect of Cologne by Anton Woensam, 1531 (City Museum of Cologne)

To date no shrinkage at all has been observed across or along the treated timbers. However, without any stabilizing treatment oakwood of the quality of the "Oberländer" wood can be expected to suffer a linear shrinkage in radial and in tangential direction of about 9 % and 20 % for the slightly degraded inner parts, and of about 15 % and 50 % respectively for the outer parts.

We were forced to interrupt the reconstruction of the medieval "Oberländer" from its stabilized boards and timbers, as is so often the case with museum work. A new boat find had to be salvaged from a building site, an early medieval river barge, dated to AD 808 by dendrochronology. It is 12 m long, 3 m wide, and it has occupied our staff for months now to find a place, means, and money to start just another large-scale two-step PEG treatment.

References

1. Grattan, D.W. and R.W. Clarke, "Conservation of Waterlogged Wood", in Conservation of Marine Archaeological Objects, ed. Colin Pearson (London etc.: Butterworths, 1987) 164-206.
2. Young, G. and I.N.M. Wainwright, "A Study of Waterlogged Wood Conservation at the Cellular Level of Organization", in Proc. Waterlogged Wood Working Group Conference, Ottawa 1981, ed. David Grattan, 107-116.
3. Watson, J., "The Applications of Freeze-Drying on British Hardwoods from Archaeological Excavations", *ibid.*, 237-242.
4. Grattan, D.W., "A Practical Comparative Study of Treatments for Waterlogged Wood. Part II. The Effect of Humidity on Treated Wood", *ibid.*, 243-252.
5. Hoffmann, P., "On the Stabilization of Waterlogged Oakwood with PEG - Molecular Size versus degree of degradation", in Proc. 2nd Waterlogged Wood Working Group Conference, Grenoble 1984, 95-115.
6. Saeterhaug, R., "Investigations Concerning the Freeze-Drying of Waterlogged Wood Conducted at the University of Trondheim", *ibid.*, 195-206.
7. Hoffmann, P., "On the Stabilization of Waterlogged Oakwood with PEG. II. Designing a Two-Step Treatment for Multi-Quality Timbers", Studies in Conservation 31 (1986) 103-113.
8. Barka, G. and P. Hoffmann, "Simultaneous Separation of Oligomeric and Polymeric Ethylene Glycols (DP1-110) Using Reversed Phase High-Performance Liquid Chromatography, *J. Chromatography*, 389 (1987) 273-278.
9. Hoffmann, P., "HPLC for the Analysis of PEG in Wood", Proc. 3rd Wet Organic Archaeological Materials Group Conference, Fremantle 1987, 41-58.
10. Hoffmann, P., "On the Stabilization of Waterlogged Softwoods with Polyethylene Glycol (PEG). Four Species from China and Korea", *Holzforschung* 44 (1990), in press.

ABSTRACT

A new method for the preservation treatment of excavated waterlogged wood is described. The new method, which consists of immersion into a mannitol solution and immersion into a PEG solution followed by freeze drying, is an improved method from the <mannitol + freeze-drying> method which is quite well known in this field. The new method gives little dimensional change to a treated waterlogged wood, and needs shorter and simpler process than the conventional one.

KEYWORDS

Waterlogged wood, Mannitol, PEG, Crystallization, Freeze-drying

A NEW FREEZE-DRYING METHOD USING MANNITOL AND PEG FOR THE PRESERVATION OF WATERLOGGED WOOD

Setsuo Imazu and Tadateru Nishiura*
Kashihara Archaeological Institute
50-2 Unebi-cho, Kashihara-shi, Nara-ken
634 Japan

Introduction

Various treatment methods for the preservation of waterlogged wood are utilized, such as consolidation with PEG, freeze-drying and impregnation with sucrose. However, these methods have some problems, such as the fact that the treatment takes much time and that the processes using organic solvents are very complicated. Thus, the authors have made researches for the development of a simpler and safer method for the preservation of a large quantity of waterlogged wood. As a result, a new effective method has been developed by improving the <mannitol + freeze-drying> method which is quite well known. Here, this new method is described.

Development of the new method (Improvement of the <mannitol + freeze-drying> method)

Mannitol has been used for the preservation treatment of waterlogged wood due to the following points of excellence.

- It consists of needle crystals.
- It is soluble in water.
- It has little hygroscopicity (See table 1).
- It has no toxicity.

Table 1. Comparison of hygroscopicity of mannitol and sucrose

	Rate of weight increase(%)	
	20°C, 60%RH(9days)	20°C, 100%RH(25days)
Mannitol	0.05	0.42
Sucrose	0.03	18.35

The procedure of the conventional method using mannitol is immersion of waterlogged wood into a saturated aqueous solution of mannitol followed by freeze-drying under vacuum [2]. In this case, the authors found by Test I that a 20% solution of mannitol at room temperature gives just as satisfactory results as when a saturated solution is used.

Test I:

Two kinds of waterlogged wood (Japanese oak whose water content is 460% and Japanese horse chestnut whose water content is 1070%) were employed as test samples. These samples were cut into cubic test pieces (30mm each for tangential and radial direction to annual ring and fiber direction). Four sets of three test pieces were immersed into a 10, 20, 30, and 40% aqueous solution of mannitol respectively for 7days. The solution of 10% and 20% were kept at room temperature, but the solution of 30% was kept at 40°C and the one of 40% at 60°C. In all cases, weights of the pieces almost reached their equilibrium states within three days of immersion in the solutions. After 7days' immersion, they were freeze-dried under vacuum (-40°C, 48hrs.). Shrinkage of the pieces after the treatments are shown in table 2 and fig.1.

This method is quite a good way, requiring no heating and using no organic solvent. However, it has the following problems which should be solved.

- 1) The surface of treated waterlogged wood is whitened with crystals of mannitol.
- 2) Fine cracks arise on treated waterlogged wood.
- 3) Waterlogged wood is not always consolidated sufficiently.

The authors considered that these problems can be solved by immersing the waterlogged wood into a PEG solution after immersion into the mannitol solution. Thus, the following test (Test II) was carried out, and good results were obtained [3].

* Tokyo National Research Institute of Cultural Properties
13-27 Ueno Park, Taito-ku, Tokyo 110 Japan

Table 2. Relation between the rate of shrinkage(ASE) by the treatment and the concentration of mannitol solution

Sample (Water content)	Concentration of aq. solution of mannitol (Temperature)	Rate of shrinkage(ASE)*	
		T	R
Japanese oak (460%)	Untreated(Nat. dry)	47.2	22.8
	10%(Room temp.)	1.3(97.2)	2.6(88.6)
	20%(Room temp.)	0.6(98.7)	0.5(97.8)
	30%(40°C)	0.7(98.5)	1.3(94.3)
Japanese horse chestnut (1070%)	Untreated(Nat. dry)	65.4	31.6
	10%(Room temp.)	-2.3(103.5)	2.3(92.7)
	20%(Room temp.)	-1.5(102.3)	0.3(99.1)
	30%(40°C)	-1.0(101.5)	0.7(97.8)
	40%(60°C)	-0.7(101.1)	1.5(95.3)

*ASE: Anti-shrinkage effect
T(R): Tangential(Radial) direction to annual ring

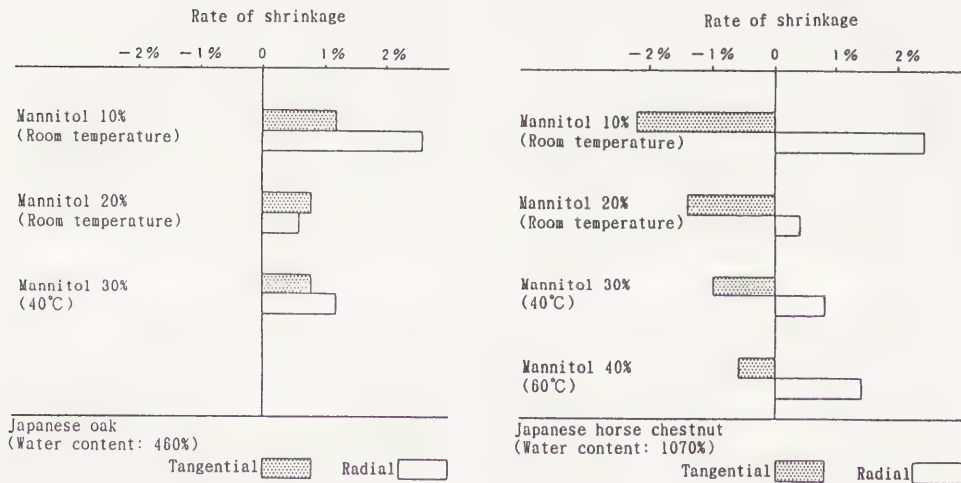


Fig.1 Relation between the rate of shrinkage by the treatment and the concentration of mannitol solution.

Test II:

An excavated waterlogged wood (Japanese horse chestnut) with a diameter of 50cm and a length of 100cm was employed as a test sample. This waterlogged wood is considered to be about 2400 years old and its water content was 580%. The wood sample was cut into cubic test pieces (30mm each for tangential and radial direction to annual ring and fiber direction). The pieces were immersed into a 20% aqueous solution of mannitol for 7days at room temperature. Then, four sets of three test pieces were immersed into a 20, 30, 40 and 60% aqueous solution of PEG 4000 respectively for 7days at room temperature. In this case, weights of the pieces almost reached their equilibrium states within three days of immersion in the solutions. Fig.2 shows the relationship between weight increase of the pieces and immersion time in a 40% solution of PEG. Finally, these test pieces were freeze-dried under vacuum (-40°C, 48hrs). As controls, three test pieces were immersed into a 60% aqueous solution of PEG 4000 at room temperature for 7days and then freeze-dried under vacuum (-40°C, 48hrs) and three other pieces were just freeze-dried under vacuum (-40°C, 48hrs); additional three pieces were dried naturally. Rate of shrinkage (ASE), bulk density and condition after the treatments are shown in table 3 and fig.3.

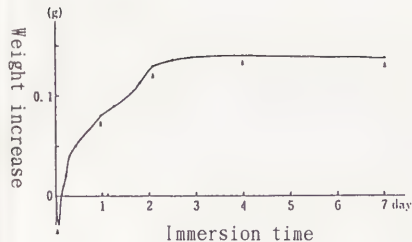


Fig.2 Weight change of waterlogged wood in a 40% solution of PEG, after immersion treatment into 20% mannitol solution for 7 days.

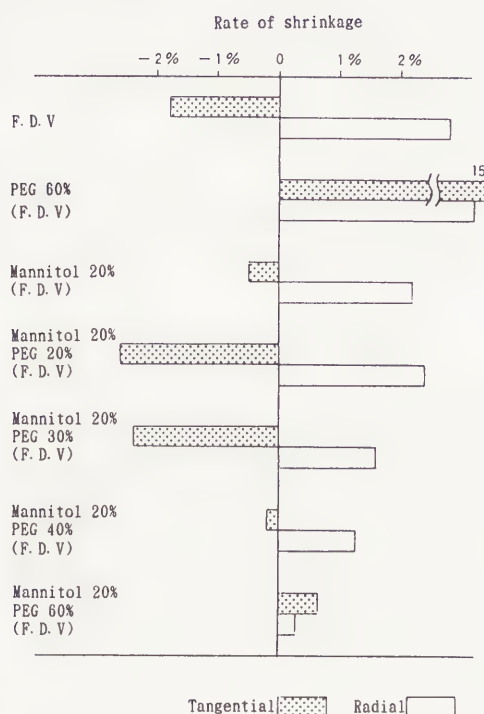


Fig. 3 Relation between the rate of shrinkage by the treatment and the concentration of PEG solution in the new method.

Table 3. Rate of shrinkage(ASE), bulk density and condition of waterlogged wood after treatment

Treatment	Rate of shrinkage(ASE)		Bulk density	Condition after treatment
	T	R		
Natural dry	56.9	27.5	0.58	Terrible shrinkage and distortion.
< F. D. V >*	-1.9(103.3)	2.7(90.2)	0.17	Numerous cracks on radial direction.
PEG 60% < F. D. V >	15.2(73.3)	3.1(88.7)	0.54	Fine cracks vertical to fiber direction. High distortion.
Mannitol 20% < F. D. V >	-0.6(101.1)	2.1(92.4)	0.31	A few cracks on radial direction. Fine cracks vertical to fiber direction.
Mannitol 20% PEG 20% < F. D. V >	-2.9(105.1)	2.3(91.6)	0.25	A few cracks on radial direction.
Mannitol 20% PEG 30% < F. D. V >	-2.5(104.4)	1.7(93.8)	0.39	A few cracks on radial direction.
Mannitol 20% PEG 40% < F. D. V >	-0.3(100.5)	1.3(95.3)	0.45	Good.
Mannitol 20% PEG 60% < F. D. V >	0.7(98.8)	0.3(98.9)	0.47	Good. (Slight distortion)

*F. D. V : Freeze-drying under vacuum(-40°C, 48hrs)

The effects of the immersion into a PEG solution are considered as follows:

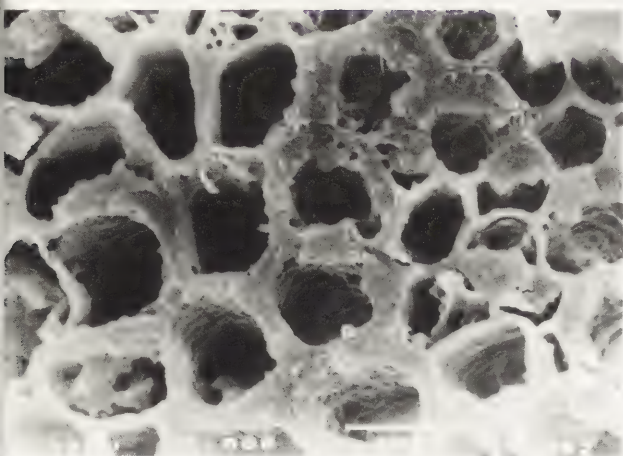
- 1) Mannitol on the wood is dissolved away in the PEG solution so that whitening of the treated wood after drying does not occur.
- 2) Impregnated PEG protects the surface of the treated wood from rapid drying during the drying process and prevents the growth of fine cracks on the surface of the wood.
- 3) Impregnated PEG gives the treated wood sufficient mechanical strength.

Observation of the interior of the treated waterlogged wood by SEM

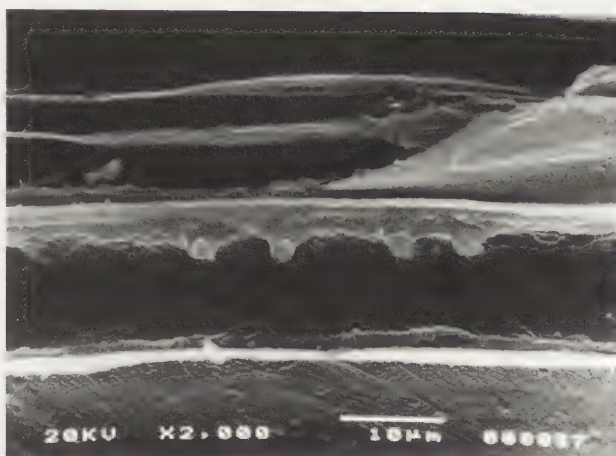
In order to investigate how mannitol and PEG are present in the treated waterlogged wood, interior of the wood was observed by SEM. And the following facts were found by the observation.

- 1) [Immersion into a 20% mannitol solution (7days) → freeze-drying under vacuum]
Mannitol crystals of 1-3μm are found adhering thickly to the surface of the inner micro-structure of the treated wood. However, there is a small amount of crystals on the surface of vessels (See fig.4(a)-(c)).
- 2) [Immersion into a 20% mannitol solution (7days) → Immersion into a 40% PEG solution (3days) → Freeze-drying under vacuum]
Mannitol crystals of 15-30μm are found adhering to the surface of the inner structure of the treated wood. Vessels are filled with crystals (See fig.4(d)(e)).
- 3) [Immersion into a 20% mannitol solution (7days) → Immersion into a 40% PEG solution (7days) → freeze-drying under vacuum]
The core part of the treated wood is filled with large size mannitol crystals. However, the rim part of the wood is not impregnated with mannitol crystals but with PEG instead (See fig.4(f)).

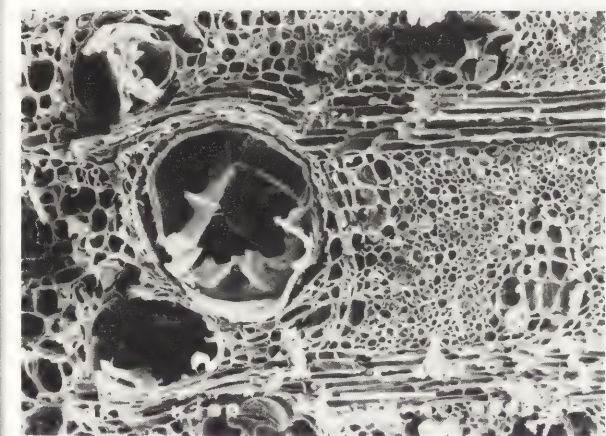
From the above facts, the high preservation effect of the new method is considered to be due to the adhesion of large mannitol crystals to the wall of the inner structure of the treated wood. And the growth of mannitol crystals within the inner structure of the treated wood seems to be due to the subsequent immersion treatment into a PEG solution which is hygroscopic, though this explanation is still in the stage of hypothesis. By long immersion in a PEG solution, however, mannitol in the treated wood is gradually replaced with PEG.



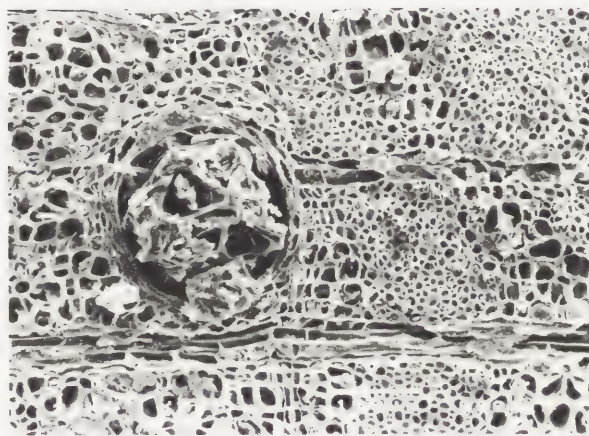
(a) Mannitol 20% → F. D. V(Cross section)
Mannitol crystals adhering to cell walls ($\times 2000$)



(b) Mannitol 20% → F. D. V(Tangential section)
Mannitol crystals adhering to cell walls ($\times 2000$)



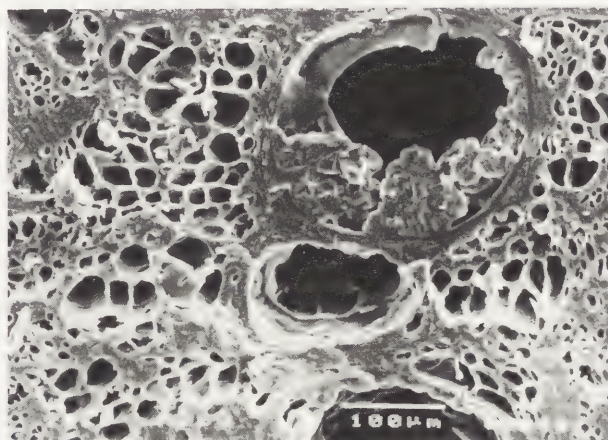
(c) Mannitol 20% → F. D. V(Cross section)
Mannitol crystals in vessels ($\times 200$)



(d) Mannitol 20% → PEG 40% → F. D. V(Cross section)
Large mannitol crystals grown in a vessel ($\times 200$)



(e) Enlarged view of (d)($\times 2000$)



(f) Mannitol 20% → PEG 40% → F. D. V(Cross section)
PEG adhering to vessel wall and shrunk mannitol crystal ($\times 200$)

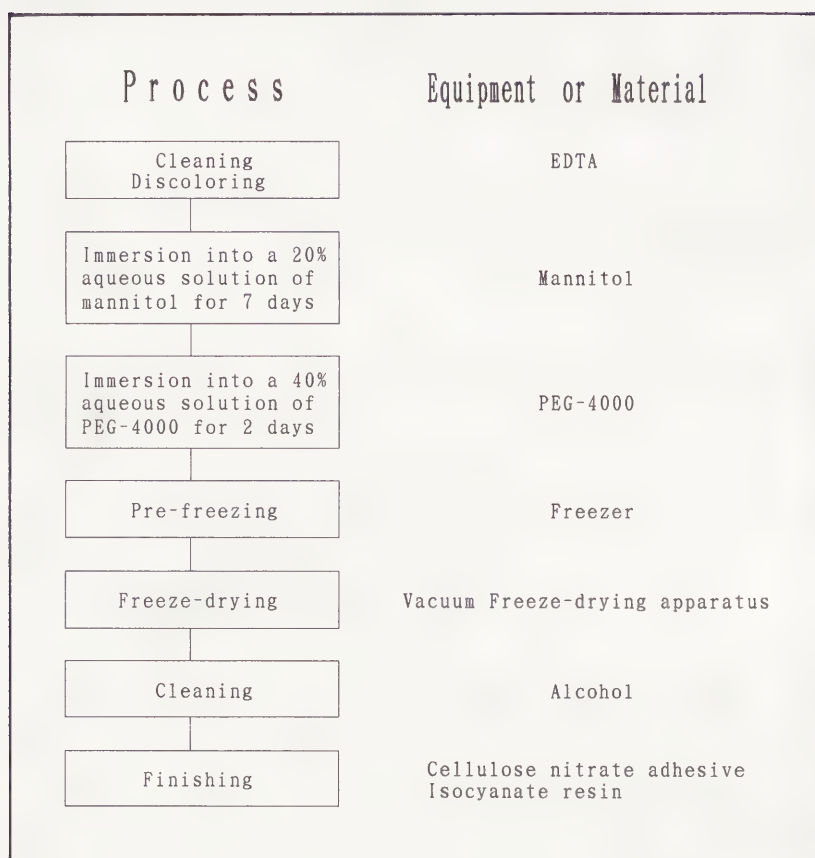


Fig.5 Practical treatment procedure for the new method.

Application of the new method

Now, in Japan, the new method is partly employed for practical use, mainly for small waterlogged woods, according to the procedure shown in fig.5. The method has been effectively applied particularly for waterlogged lacquer wares, because the method needs no organic solvent, almost no artificial heating and relatively little time for total treatment.

Conclusion

A freeze-drying method using mannitol and PEG has been developed as a new, simple and effective method for the preservation treatment of waterlogged wood. The method does not have the defects which the conventional <mannitol + freeze-drying> method has. The improvement is dependent upon immersion into a PEG solution after immersion into a mannitol solution and before freeze-drying. The method is effective particularly for small and fine artifacts which are excavated in a waterlogged condition.

REFERENCES

1. C.A.Browne, "Characteristics of Mannitol," *Journal of Industry, Engineering and Chemistry* 14 (1922): 712.
2. H.Murray, "The Use of Mannitol in Freeze Drying Waterlogged Organic Material," *The Conservator*, no.9 (1981): 33-35.
3. S.Imazu, "The Method Using Mannitol and Polyethylene Glycol in Freeze Drying Waterlogged Organic Material," *Kobunkazai no kagaku (Scientific Papers on Japanese Antiques and Art Craft)*, no.33 (1988): 52-62.

ABSTRACT

It is shown that for characterizing wood degradation degree the ratio of cellulose percentage to lignin one is reliable. A method for the calculation of the ratio based on the IR-Fourier transform spectroscopic data with their following mathematical treatment is suggested. The method is suitable for wood of different species and degradation degree.

KEYWORDS

Archaeological wood, fourier-transform spectroscopy, cellulose, lignin

QUANTITATIVE ESTIMATION OF ARCHAEOLOGICAL WOOD DEGRADATION DEGREE BY INFRA-RED FOURIER TRANSFORM SPECTROSCOPY

A.I. Kirillov
State Hermitage Museum
191065 Leningrad, USSR

E.A. Mikolajchuk
State Hermitage Museum
191065 Leningrad, USSR

One of the key problems in the restoration of archaeological wood is the degree of its degradation, as it is this, that the choice of the method and the preparations for the treatment of the object depend upon. That is why, it is very important to find a way permitting a quantitative estimation of the state of the article to be treated. The validity of the method selected should, apparently, be evaluated proceeding from the following three criteria: its reliability, the minimum amount of the sample necessary, and the time necessary for the analysis.

The physical and mechanical properties of the archaeological wood stand in marked contrast to those of sound wood due to the considerable changes of the chemical composition which archaeological wood undergoes in the process of aging. In our opinion, the age of the sample should not be used as a criterion of its state, as the latter depends largely upon the keeping conditions, species of wood and some other factors. Therefore, a search for a more objective parameter is required.

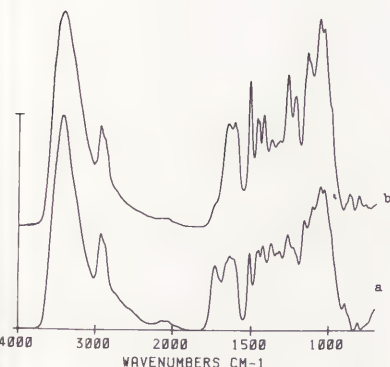
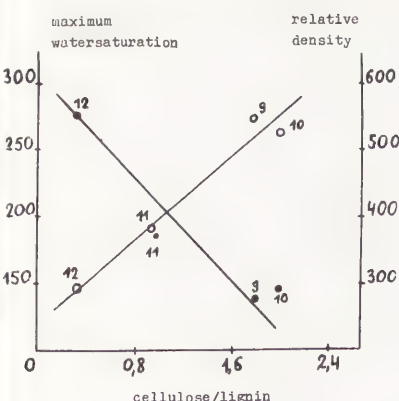
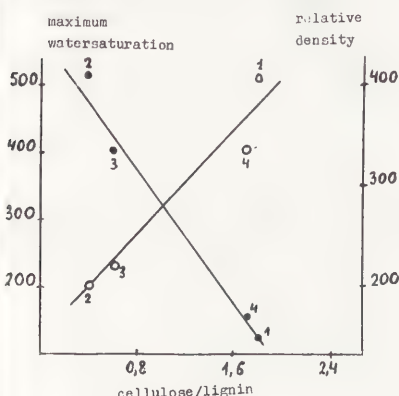
Owing to the fact that the destruction taking place in the process of aging affects to a greater degree the cellulose forming a part of the wood, and in a considerably lesser degree - the lignin part, there is some reason to believe that the value of the concentration ratio cellulose/lignin can serve as a reliable enough quantitative characterisation of its state. The data, given in Fig.1 (9 - sound oak, 10-12 - archaeological oak; 1 - sound pine, 2-4 - archaeological pine) supports this assumption. In fact, a good correlation can be observed between the ratio in question and such physical properties of the objects as the maximum water saturation and relative density (the ratio value cellulose/lignin is calculated by using the percentage of Kürschner's cellulose and lignin in wood determined according to routine procedures. Thus, the task is to find a method for determining the relative content of cellulose and lignin in wood that could be considered adequate proceeding from the three above mentioned criteria.

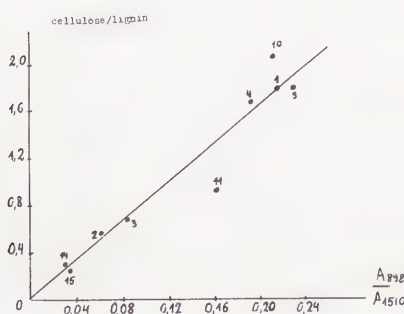
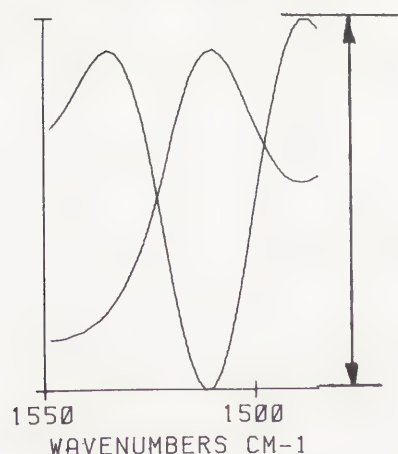
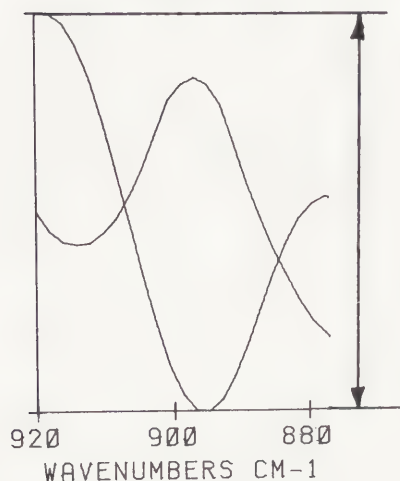
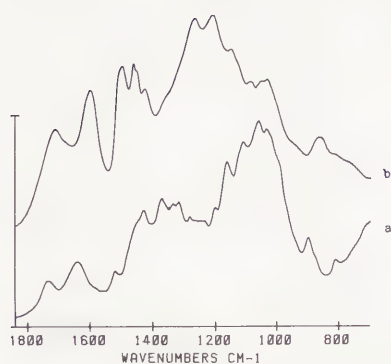
The chemical method of analysis, widely used at the present time and being quite reasonable in terms of the reliability of the results obtained, has a very essential defect - it requires a considerable bulk of wood (40g). Besides, this method of analysis takes rather much time. All this makes it necessary to look for some other ways to solve the problem.

In particular, applying infra-red spectroscopy looks promising. It is widely applied in studying cellulose, lignin and wood itself.

In developing the spectroscopic method, samples of sound present day oak, sound present day pine, as well as samples of archaeological wood - pine, oak and birch - were utilized. All samples were dried to their constant mass. A 10mg sample of the wood mass was mixed with 150mg calcium bromide, put into a vibromill where it was mixed thoroughly during 5 minutes. Pressing in vacuum under 5000kg/cm² pressure followed. The infra-red spectra were obtained with the help of Fourier-spectrophotometer IFS-85 of the firm "Bruker" Fig.2: a) sound and b) archaeological pine wood.

IR-Fourier transform spectroscopy provides considerably higher sensitivity of the method, which gives the opportunity to analyse samples of microscopic dimensions. Besides, the velocity of spectrum measurement is essentially increased and the mathematical treatment of results (spectra differentiation, in particular) becomes much easier due to the installed computer. The data interpretation does not cause additional difficulties because the measurement final result is as ordinary IR-spectrum. The whole process of the measurement and the calculation does not take more than one hour.





The study of the IR-spectra obtained was aimed at finding some parameter permitting the estimation of the ratio value cellulose/lignin in samples with the view of comparing the results with those received by means of chemical analyses and preparing the standard straight line. The quotient got from the division of the amplitudes of the analytical absorption band second derivatives was taken as such parameter. This choice is due to the fact that the utilization of the second derivative permits transition to the quantitative analysis without employing the basis line method which, in our opinion, does not always lead to correct results. Besides, double differentiation of the spectrum permits reducing the errors brought in by the contribution of dispersion and that of the neighbouring absorption bands into the amplitude of the band in question.

As analytical, we selected some bandes whose attribution seems reliable enough. They are: the absorption band 1510cm^{-1} which arose from the fluctuations of aromatic nuclei in lignin, and the band 898cm^{-1} characteristic of carbohydrates. The former was applied for the quantitative characterization of the lignin content in the samples, the latter - for cellulose content (the investigated parts of the cellulose by Kürschner a) and lignin b) spectra received from the wood of sound pine are given in Fig.3). As an example, the above analytical bands and the second derivatives taken from IR-spectrum of one of the samples are shown in Fig.4.

Fig.5 illustrates the results obtained from the comparison of the ratio values of cellulose/lignin, calculated on the basis of the chemical analyses data (plotted as ordinate) and of the spectroscopic study (plotted as abscissa) for various objects. A quite satisfactory correlation can be observed and permits, in our opinion, to employ the straight line as a standard in determining the ratio value cellulose/lignin in archaeological wood samples by the spectral analysis method; an important factor being the universality of the standard line - the results relating to the wood of various species: oak, pine, birch get within the limits of a single relationship.

Conclusion

1. The ratio cellulose/lignin can be used as a characteristic of archaeological wood degradation degree.
2. The problem of rapid and reliable calculation of this ratio may be solved with the help of TR Fourier transform spectroscopy.
3. Suggested method is suitable for wood of different species and degradation degree.

ABSTRACT

Sucrose conservation of 15-16th c. waterlogged wooden finds was done. The objects were made of European spruce, pine and oaks.

The conservation began in 50 g/l sucrose solution in water, the final concentration was 1050. The bath was kept at room temperature during the whole conservation period. The impregnation solution contained sodium-pentachlorophenol and formaldehyde to prevent growth of microorganism. After reaching the final sucrose concentration an impregnation period of 3-15 months followed. Then the objects were washed with tap water and wrapped up in canvas and buried in sand for drying.

The objects conserved have kept the natural colour, appearance and touch of the sound wood. The dimensional stabilisation was excellent.

The broken parts were glued by epoxide resin and the wood-complementation was done by the mixture of the same resin, solvent, saw dust, earth pigments, chalk and titanium di-oxide.

KEYWORDS

waterlogged wood conservation, sucrose-conservation, wood complementation

THE SUCROSE CONSERVATION OF 15-16th c. WATERLOGGED WOODEN FINDS

András MORGÓS

National Centre of Museums, Conservation Department
H-1087. BUDAPEST, Könyves Kálmán krt. 40

Lucia GLATTFELDER-McQUIRK

Archaeological Inst. of the Hungarian Academy of Sciences
H-1250. BUDAPEST, Uri u. 49.

1. Introduction

Archaeologist Zs. Miklós excavated a well in a former monastery of the Order of St. Paul in Márianosztra in 1985. The well dates back to the second half of the 15th and the first half of the 16th century. The timber construction of the well and many objects for personal use were found in the well e.g. buckets, boot-stretchers, pots made of bark, troughs and other wooden fragments.



Figure 1. Wooden finds found in the well before conservation



Figure 2. Wooden finds found in the well before conservation

The majority of the objects is made of European spruce (*Picea abies*); pine (*Pinus silvestris*) and European oaks (*Quercus petraea* and *Quercus robur*).

As a method for the conservation of the wooden finds in the well the sucrose conservation method was chosen. We have published information already earlier about the sucrose conservation: previous literature, the method applied by us, the results thereof, the scanning electron microscopical examinations made by us and the advantages of the method (1).

2. Experiments and conservation method applied

The objects were kept in water from the time of excavation until conservation. All the objects appointed were sent for analysis to determine the species of wood. The finds chosen for treatment were marked by aluminium number-plates. The change of mass was continuously measured in the course of conservation and drying. The average water content of the objects was deter-

mined (spruce, pine 305-350% oaks 350-450%). Microbiological control was kept of the conservation solution.

The conservation was done in the following way:

We put the waterlogged wood into a 50 g/l sucrose solution in water. The concentration of the solution was given in g sucrose/l water. The quantity of water in the samples was ignored.

To prepare the conservation solution we used crystalline beet sugar. The quality of this is defined by the Hungarian Standard No. 3671. The sugar used contained 99.75% sucrose, determined by polarimeter, maximum moisture content 0.10% and insoluble matter context max. 50 mg/kg.

The impregnation solution contained 1% (w/v) sodium-pentachloro-phenol and 2% formaldehyde to prevent growth of microorganisms. The bath was kept at room temperature during the whole conservation period. Every 2 or 3 days the concentration was raised by 50 g/l sugar. After 750 g/l concentration we continued to put the sugar into the bath, but we waited until previously added sugar had dissolved. Stirring was not necessary. The final sugar concentration was 1050 g/l.

The period of impregnation was from 3-15 months depending on the thickness of the objects. The conservation of objects with a thickness of 1-1.5 cm took 3-5 months, while in the case of the objects with a thickness of 8-10 cm took 15 months. The conservation of the large timbers found in the well is still going on due to their size.

After impregnation the objects were washed with tap-water and then wrapped up in canvas and buried in sand. The conserved wooden objects were dried in sand for 10 months until they reached constant weight.

The objects conserved have kept their original colour, appearance and touch. By the conservation, we reached good dimensional stabilization. To take an example, the iron rings holding together one of the stave buckets found in the well could be reallocated on the bucket after conservation and fitted perfectly.

The results of the mass change during conservation did not show a clear cut tendency. On this basis some further examinations are needed.

The conservation method applied is cheap as it does not need any special equipment, or heating, or expensive chemicals.

The objects conserved could be glued and complemented in a very good way. The most adhesives - recommended for sound wood - are suitable for gluing. We chose epoxide resin adhesive (UVERAPID 20, produced by UVESZ GMK, Hungary). The complementation of the missing wood parts was made by the mixture of the same epoxide resin, solvent (e.g. acetone), saw dust, earth pigments, chalk and titanium di-oxide. This complementary material sets between 1-3 days depending on the quantity of solvent. The complements can easily be shaped prior to setting by scalpels or chisels.

The complements if needed can be retouched or painted.

The appearance of the complements can be made comparable to the original appearance of the wood by tempera using hatching, so the completed part is distinguishable from the original on close inspection only.



Figure 3. Some of the finds after conservation

References:

1. A. Morgós; L. Glattfelder-McQuirk; E. Gondár: The cheapest method for conservation of waterlogged wood: the use of unheated sucrose solutions. ICOM Comm. for Conservation. 8th Triennial Meeting, Sydney 1987. Preprints 313-319.

ABSTRACT

During conservation of a wooden boat, surplus polyethylene glycol (PEG) was melted away. On cooling, the PEG divided itself into three distinct phases: solid, pasty and liquid. These fractions resulted from a rapid oxidative degradation of PEG in warm air. Dry polyethylene glycol degrades significantly within four hours when heated to 75°C. Water protects against degradation, which is perhaps why the phenomenon has not been described before in the conservation literature.

KEYWORDS

Waterlogged wood, polyethylene glycol, PEG, oxidation, degradation.

DECOMPOSITION OF POLYETHYLENE GLYCOL (PEG) ON HEATING

Tim Padfield, Janne Winsløw, Walter Batsberg Pedersen* and Jens Glastrup**

The National Museum of Denmark
Department of Conservation
Brede, DK-2800 Lyngby, Denmark

*
Risø National Laboratory
Postbox 49
DK-4000 Roskilde, Denmark

Introduction

The Hjortspring boat was discovered in the beginning of this century in south Jutland and excavated in the early twenties. It is one of the oldest dated boats in the world, about 400 BC. It was, after numerous conservation attempts, most recently conserved in the sixties by impregnation in polyethylene glycol 4000. The boat was discovered in fragments. After the final impregnation the thousands of pieces were left embedded in slabs of solid PEG. Later they were released by placing the slabs in an oven at 80°C for a few hours. The PEG that melted into the tray below, separated into three fractions, one solid, one pasty and a third that was still liquid at room temperature. We suspected that the PEG had partly decomposed at some point in the long conservation process. This paper describes the work done to explore the nature of the decomposition process.

Analytical methods

Thin Layer Chromatography (TLC): This was performed on Silica gel 60(F254) microplates from Merck. The mobile phase was chloroform/methanol/water (6/50/24). The samples were run in a small beaker covered with parafilm. Developing was done by spraying with a 0.005N iodine in potassium iodide solution. To improve visibility the plates can be dried and sprayed with a 0.2% starch solution(1).

Size Exclusion Chromatography (SEC): The samples were dissolved in tetrahydrofuran (THF). 50µl of the solution was injected into a column system comprising a 1000Å, a 500Å and a 100Å column, all from Polymer Laboratories. The chromatographic separation was performed at room temperature by pumping THF through the columns at a flow rate of 1ml/min. The composition of the eluate was monitored by a differential refractometer. A series of PEGs with different molecular weights were chromatographed in order to establish the calibration.

Materials

PEGs of various molecular weights were obtained from Hoechst. The PEG 4000 used in the experiments was dried by bubbling dry pure nitrogen through it. The nitrogen, Quality M from Air Liquide, was passed over a molecular sieve 3Å, Merck, art. 5704, then through the molten PEG at 60°C for 16 hours.

Room air was filtered through glass wool and active carbon filters then dried with silica gel and molecular sieve.

Approximately 76% relative humidity (RH) was maintained over the humid sample (water content 6.5%) by first equilibrating silica gel at room temperature over a saturated sodium chloride solution. This gives an equilibrium RH of 76%. This gel was transferred to a cylinder inside the oven, through which passed a slow stream of dry air at the desired temperature. The equilibrium relative humidity over silica gel is only slightly affected by temperature and the relative humidity can therefore be assumed to be almost the same at high temperature. Fig. 1 shows the experimental system.

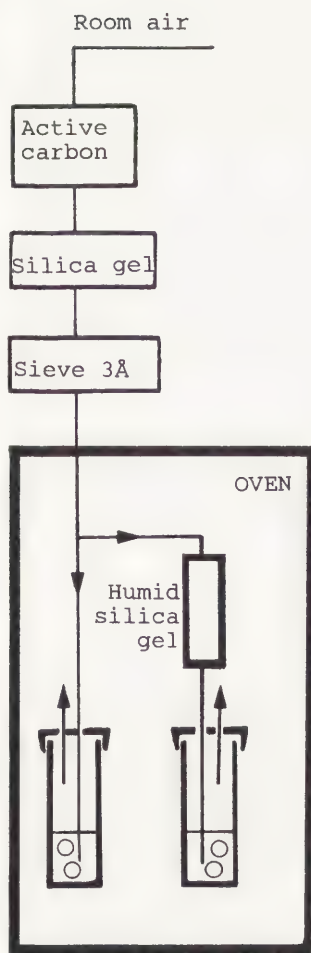


Fig. 1: Experimental system. Dry, filtered air is pumped into one reaction flask. The supply to the other passes through a column of silica gel preconditioned to 76% RH at room temperature.

** Author to whom correspondence should be addressed

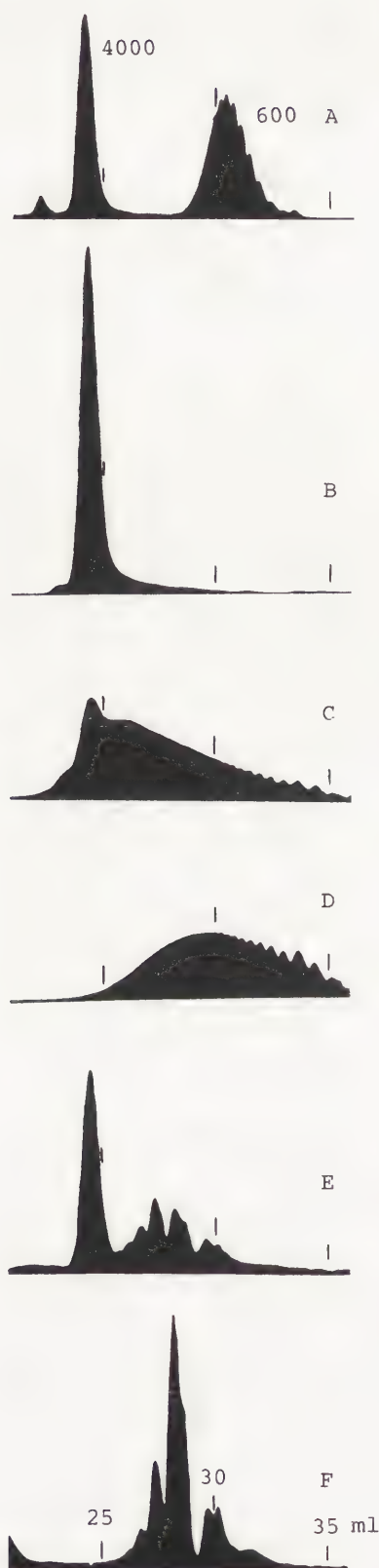


Fig. 2: SEC chromatograms of samples taken before and after melting off the PEG from the boat.

A: Standard made by mixing PEG 4000 with PEG 600. B: The hard fraction found in the tray after melting and cooling. C: The pasty fraction. D: The liquid fraction. E: A sample of PEG taken from the boat before melting. F: A sample of pure beeswax.

Experimental

The first indications of PEG 4000 degradation came from the fractionation of the material after melting off PEG from the boat. We first confirmed that this material was decomposed PEG by analysing the three different fractions using SEC. The chromatograms are shown in fig. 2B-D. A mixed standard of PEG 4000 and 600 is shown in 2A. Fig. 2C, which represents the chromatogram of the intermediate sample, demonstrates the presence of both a surviving PEG 4000 fraction and decomposed material.

To prove that significant decomposition occurred during the brief heating period, a sample of PEG was taken from an unheated fragment of wood. The chromatogram is shown in fig. 2E. The minor peaks in the 30 to 35ml region could well be material originating from decomposed PEG. However, the broad shoulder seen in fig. 2C is not seen and is replaced by irregular peaks which probably originate from beeswax, previously used on the boat. Fig. 2F shows a chromatogram of pure beeswax, which resembles the additional peaks in 2E.

We succeeded in decomposing PEG 4000 in the laboratory by simply heating fresh, dried PEG in an oven at 75°C without any special humidity control. This corresponds to 2-3% RH. Samples were taken at intervals between 2 and 120 hours and analysed by TLC. The results are shown in fig. 3B. They show that the PEG, under constant heating at 75°C, rapidly changes in composition. Already after four hours the initially sharp peak defining the fresh PEG shows tailing, demonstrating the formation of components of lower molecular weights. After 16 hours there is virtually no trace left of the original material. This can be seen by comparison with the standards, pure PEG's ranging in average molecular weights from 600 to 20,000 Daltons, shown in fig. 3A.

We were surprised that such a short exposure to heat caused such damage to a material that is held warm for long periods during impregnation of wood. It could be that water, always present during the impregnation process, has a stabilising effect on the PEG.

We therefore set up an experiment in which PEG samples were heated both in dry air and in air in which the relative humidity was approximately 76% at 75°C. Samples were taken out for TLC analysis after 20 hours exposure. We also analysed a sample of PEG 4000 which had been heated under nitrogen. The results are shown in fig. 4. They clearly demonstrate that the PEG decomposed detectably only in dry air. The sample kept under nitrogen showed no sign of degradation. It therefore seems reasonable to conclude that the decomposition noticed during heat treatment of the Hjortspring boat was the result of oxidative degradation caused by oxygen in the absence of water.

Discussion

Our investigations confirmed that the PEG had decomposed and that the decomposition occurred during the brief melting process while handling the wood. A control sample taken directly from the unheated wood showed no detectable breakdown (fig 2E). There had therefore been little damage to the PEG during the long period in hot aqueous solution, nor in the 25 years of its existence in an ordinary room climate.

These experiments show clearly that PEG 4000 can degrade disturbingly fast. This is in sharp contrast to expectations based on work with PEG under normal conditions.

We have not been able to find any literature describing this degradation process in the museum environment. Likewise a search in Chemical Abstracts, back to 1967, gave no results. The work presented here has been confirmed by the Hoechst company (2,3). They, however, used a much higher temperature and a sealed reaction vessel. Under these reaction conditions water was not so effective in protecting PEG, only halving the reaction rate, whereas our results indicate a more complete inhibition. Hoechst also drew our attention to research by Dulog (4) on the instability of polyglycols. This work starts with the words: "Es ist seit langem bekannt, daß niedermolekulare Äther unter milden Bedingungen mit molekularem Sauerstoff reagieren", ("It has long been known that, under mild conditions, the lower molecular weight ethers react with molecular oxygen"). He in turn mentions the thorough work of Riecke and coworkers from the thirties to the sixties (5).

TLC of PEG.

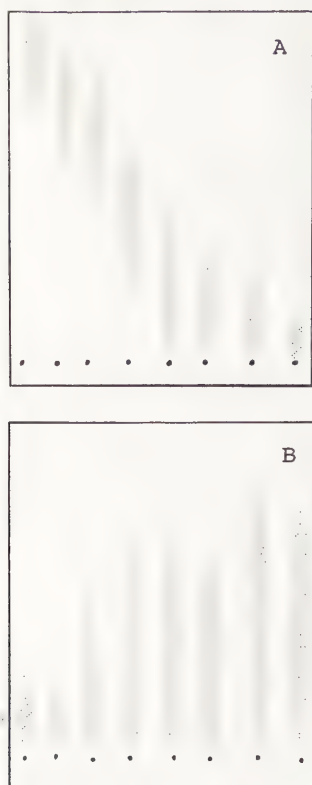


Fig. 3:

A: Chromatograms of samples of PEG of different molecular weights ranging from 600 to 20.000.

PEG standards, from left:
600, 800, 1000, 2000, 3000, 4000,
6000, 20000.

B: TLC chromatograms of PEG dry heated in an oven at 75°C, from which samples were taken at different times.

Samples, from left (hours):
0, 2, 4, 8, 16, 32, 64, 120.



Fig. 4: Influence of different atmospheres on PEG breakdown.

From left:
Standard PEG 4000
Standard PEG 800
PEG 4000 heated in nitrogen.
PEG heated in dry air.
PEG heated in humid air.

This information has some important implications for work with PEG. Surplus PEG on wood is often removed by melting. This inevitably reduces the local RH to a negligibly small value. Small pieces of wood are joined with molten PEG or with "hot melt compounds". These processes should therefore ideally be done under warm nitrogen instead of air.

It can be argued that the oxidation is of minor importance when we talk about wood filled in all pores with PEG, because diffusion of oxygen into the interior is slow. However, PEG is also used to reduce distortion during freeze drying, and here it is more susceptible to oxidation because of the open pore structure in the treated wood. On the other hand, it may be that the close association of the PEG molecules with the lignin/cellulose molecules may alter its susceptibility to degradation.

It should be noted that the oxidation products include esters and aldehydes (3), which in turn may be harmful to wood.

Further work should include measuring the activation energy of the oxidation reaction and from that the approximate oxidation rate at room temperature. Furthermore it is important to measure the relative humidity dependency of the reaction, which may give an indication of the climatic conditions under which PEG conserved objects are best preserved.

Finally it should be kept in mind that this degradation is a result of an oxygen attack on an ether bond. There is therefore a risk that other polyglycols such as polypropylene glycol are also susceptible to this breakdown process.

References

1. K. Thoma, R. Rombach and E. Ullmann, *Scientia Pharmaceutica*, 32, 1964, p. 216.
2. Glass, "Thermooxidatives Verhalten von polyethylenglycol 8000 $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, der Einfluß von Wasser und Butylhydroxyanisol in Sauerstoffbombentest(DIN51780)", Prüfbericht, Hoechst, 1989. Unpublished.
3. Stankoviak, Glaß, "Thermooxidativer Abbau von Triethylenglycol", Forschungsbericht, Hoechst, 1987, unpublished.
4. L. Dulog, "Oxidation von Polyepoxiden mit molekularem Sauerstoff", *Farbe und Lack*, 73, no. 1, 1967, 11-17.
5. A. Riecke, "Über Peroxyde der Äther, der Carbonyl-Verbindungen und die Ozonide", *Angewandte Chemie*, 70, no. 9, 1958, 251-266



Working Group 8

Photographic Records

Documents photographiques



ABSTRACT

The conservation of painted photographs has to consider those factors relating to the photographic properties of the image as well as those conditions that can be dealt with by conventional fine art conservation techniques. The restoration of three painted photographs from the collection of the 'Höhere Graphische Bundeslehr- und Versuchsanstalt' in Vienna, dating from 1854 to 1900, is described. The treatments include inpainting, surface cleaning, consolidation treatments and matting. In addition to the conservation treatments an accelerated ageing test is described, which was conducted in order to find suitable retouching media for silver-containing photographic images on paper. The results of this investigations were used in the above-mentioned restoration treatments.

KEYWORDS

PAINTED PHOTOGRAPHS, SILVER PROCESS, INPAINTING, ACCELERATED AGEING, SALTED PAPER PRINT.



Figure 1
Torres Hermanos: Portrait of an Unknown Man; before treatment, raking light.

THE CONSERVATION OF PAINTED PHOTOGRAPHS

Klaus B. Hendriks and Sebastian Dobruskin

National Archives
of Canada
395 Wellington Street
Ottawa, Ontario
Canada, K1A 0N3

National Library
of Austria
Josefsplatz 1
A-1010 Vienna
Austria

Introduction

Consolidants and retouching media are required in the conservation of photographs in general and especially in the restoration of hand coloured photographic prints.

An accelerated ageing test was therefore conducted in order to find appropriate retouching media for silver based photographic images. The results of this ageing test, which are briefly described at the end of this paper, were then used in the actual restoration of three painted photographs from the collection of the 'Höhere Graphische Bundeslehr- und Versuchsanstalt' in Vienna.

Conservation treatment of the 'Portrait of an Unknown Man'

This portrait was taken by the Mexican artists Torres Hermanos (Torres brothers) and dates before 1900. It is a salted paper print, painted with water colour. The background colour was applied using an air brush technique. A remarkable aspect of this image is that it is pasted onto an embossed brass sheet, showing the relief of the photographed man (Fig. 1).

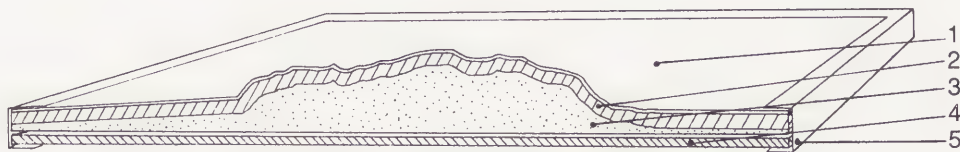
Apart from the basic attempt to preserve the art work, the conservation treatment was aimed at making its photographic technique more approachable, because it is still part of a photographic study collection.

Therefore the mat board had to be removed. It was attached on the reverse with paper strips cut from a receipt form of the library of the Höhere Graphische Lehr- und Versuchsanstalt and an order form from a Viennese wine dealer. With these paper strips the last matting can be dated around 1910. The adhesive of these paper strips was softened with a sodium carboxymethylcellulose* poultice.

After removal of the paper strips the mat lay loose on top of the original. However, adhesive coatings and ripped-off parts of the mat board, as well as parts of the original indicated that this mat had been pasted at least two times directly onto the surface of the photograph and later torn off again (Fig. 2).

Areas of loss on the photograph itself showed that the thin salted paper was pasted onto a yellowish metal sheet, which was identified as brass. White traces on the verso indicated that the embossed metal sheet was filled with gypsum (Fig. 3).

The residual adhesive, probably wheat starch paste, was very hard to remove. Parts of the original, water-soluble, colours had been dissolved by the paste. A sodium carboxymethylcellulose poultice was applied again to swell the paste, which was then slowly removed with a scalpel.

**Figure 3**

Schematic Cross Section

1: Painted salted paper print
4: Cardboard

2: Embossed brass plate
5: Edge binding (paper)

3: Gypsum

* In all the following cases: Cellofas B-3500 (R)



Figure 2

Torres Hermanos: Portrait of an Unknown Man; during treatment after the removal of the window mat, which was adhered at least twice to the surface of the photograph and torn off again.



Figure 4

Torres Hermanos: Portrait of an Unknown Man; after retouching with selected Winsor & Newton Artists' Watercolours.

Because of the extreme sensitivity of the water colour, only the main part of the paste could be removed using this technique. The residual paste was reduced by swelling it for a few seconds and then blotting off the poultice together with the dissolved adhesive. The adhesive could be reduced to a very thin layer, using this technique. The parts of the photograph that had been torn off were, as far as they were present, transferred from the verso of the window mat to the original, using wheat starch paste as an adhesive. The remaining losses were filled with a mixture of sodium carboxymethylcellulose and paper fibers of similar paper. This mixture was applied and smoothed down with a dentist's tool.

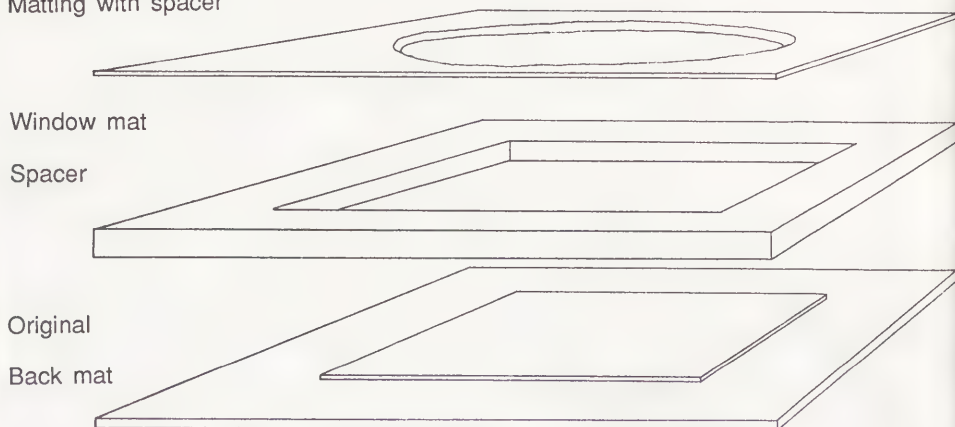
It was decided to leave one small loss unfilled in order to show that there is a brass sheet underneath the paper of the photograph, because it is part of a photographic study collection.

For the inpainting of the losses 'Winsor & Newton Artists' Watercolours' (in tubes) were used, but only those which showed no reactions on salted paper during the accelerated ageing tests, which are described later (Fig. 4).

It was decided not to use the old window mat since it had covered the signature. Instead, a new grey window mat was cut, using acid free board. The format was enlarged to 40 x 50 cm to fit the size of the collection's standard frames. A spacer, one centimeter in thickness was inserted between the window mat and the back mat to avoid contact of the original with the window mat (Fig. 5).

Figure 5

Matting with spacer



Conservation treatment of the 'Death Portrait of Dr. Petrus'

This photograph, also a salted paper print, was taken by the Austrian photographer Albin Mutterer in 1854 (Fig. 6). He had his studio in Vienna, was born in 1826 and died 1873 after an ethanol bottle exploded in his studio¹.

Mutterer was quite famous for dragging dead bodies in his studio where he took a photograph, which was then skillfully retouched by his assistant, who made the sitter look alive. This macabre procedure was finally forbidden by the imperial authorities²³.

This salted paper print was painted over with water colour and gouache. Parts of the background were coloured in pastel technique which only survived in the areas covered by the mat board (Fig. 7). The shadows were deepened by coating them with a thin, glossy, layer of binder, probably gum arabic (Fig. 8). This old technique was used to colour etchings before the invention of photography.

It is hard to tell if there is any photographic image left to look at, but brown-violet shadows are probably part of the photographic silver image.

The window mat was attached on its verso to the cardboard of the photograph with paper strips, which were removed as described above, using a sodium carboxymethylcellulose poultice.

Under the microscope it could be observed that a fine network of cracks had developed in those parts of the shadows where the binder had been applied too thickly. Some paint losses had also occurred.

During the search for a consolidant for the flaking paint various cellulose esters were tested, because it was intended to avoid any adhesive which would have added new tension to the photograph: all water-based consolidants tested swelled the old binding medium, which then showed high gloss after drying. Finally Klucel G (R), dissolved in ethanol, was used.



Figure 6
Albin Mutterer: Death portrait of Dr. Petrus (1854); after the removal of the window mat.



Figure 7
Albin Mutterer: Death portrait of Dr. Petrus (1854); detail, condition of the deteriorated light blue background in pastel technique, which survived underneath the window mat, cracked colour layers in the dark areas, where binding medium was used to darken the shadows.

The losses were retouched, using the Winsor & Newton Artist's Watercolours (R) which had previously been tested.

To keep the original ensemble of window mat and photograph - and to make it ready for exhibition at the same time, a special matting technique was used (Fig. 9).



Figure 9
Albin Mutterer: Death portrait of Dr. Petrus (1854); after treatment, matting while keeping the original window mat.

Conservation treatment of the 'Portrait of Miss Mutterer'

The third photograph treated was another photograph by Albin Mutterer, the portrait of his daughter, taken in 1866. It is very likely that Miss Mutterer was still alive when this portrait was taken, but the photographic process and the painting technique is similar to the one used in the portrait of Dr. Petrus. Miss Mutterer's face, compared with Dr. Petrus' is less painted over, probably because there was no reason to do so: Miss Mutterer was still alive. Her face now appears very pale because the photographic image has faded partially with time (Fig. 10).

Besides a little spot of binding medium on the nose tip of Miss Mutterer, a great amount of surface dirt could be observed, which could not be removed just by gentle brushing of the surface⁴. The amount of surface dirt became more obvious after the removal of the window mat, using the same technique as described before.

This problem was solved after an intensive microscopic examination of the surface. It was found that the photographic image was covered with a relatively thick layer of binding medium to prevent the watercolours from sinking into the paper or to stop them from feathering. This technique is well described in early 'how to paint photographs' literature^{5/6/7}. The water colours themselves sank into the top layer of the binding medium and are therefore very stable against abrasion. Considering all these factors, it was decided to use an eraser to dry-clean the surface⁸. The PVC eraser 'Staedtler, Mars Plastic' No. 52650 (R) was chosen for this purpose according to analytical examinations of the Canadian Conservation Institute⁹ (Fig. 11).

After the dry-cleaning was successfully completed, the binding medium droplet was reduced using a sodium carboxymethylcellulose poultice, which was blotted off after some seconds.

Some small losses, probably caused by the appetite of some insects, were retouched using again tested Winsor & Newton Artists' Water Colours (R).

Again the old window mat was conserved and re-used. The use of the Japanese Karibari technique allowed a backing to be applied to the embossed window mat to give it more support and to keep the mat flat, without destroying the embossment (Fig. 12).



Figure 8

Albin Mutterer: Death portrait of Dr. Petrus (1854); detail, cracked colour layers in the dark areas, where binding medium was used to darken the shadows.



Figure 10

Albin Mutterer: Miss Mutterer (1866), hand coloured salted paper print, matted in embossed and gilded window mat; before treatment.

The accelerated ageing test

Results gained from permanence tests of consolidants and retouching media for works of art on panels, canvas or paper can be adapted for the conservation of photographs. Above all, one must take into account the greater sensitivity of the photographic image: it can be altered through chemical reaction, or even destroyed, by the conservation materials applied.

Although it was known quite early that certain pigments and binding media can influence the permanence of photographic images¹⁰, no systematic examination of pigments and binding media in conjunction with photographic images has been published except for Larry Feldman's article¹¹, which examines the effect of wall and furniture paint. Therefore some binding media, selected pigments and some commercially available photo retouching sets were tested under accelerated ageing conditions to find out if they would react with the photographic silver image. Since pure pigments cannot be attached to photographic test samples, corresponding Winsor & Newton Artists' Water Colours were selected.

Over 500 test samples with a gray scale were produced using the following three photographic techniques: salted paper prints, albumen paper prints, silver gelatin developed-out prints.

These samples were coated with the selected consolidants and retouching media. To obtain comparable results, it was decided to use already defined standards for accelerated ageing used by the photographic industry. The Standard ANSI PH 1.53-1986¹² from the American National Standard Institute describes an appropriate ageing test, the so called 'photo activity test' (PAT)*. Its main characteristics are: 86 % relative humidity at 50 °C for a period of 30 days.

After the accelerated ageing was completed, the samples were examined, compared with their control sample, and described, using a stereo microscope at magnifications between 8 to 32 times.

The recommendations in the tables I-VI are based on the above mentioned accelerated ageing tests¹³. Materials which are *not recommended* showed strong reactions with at least one of the three silver-containing images (salted paper prints; albumen paper prints, gold toned; silver gelatin print). Materials rated as *adequate* showed little or very small reactions and can, in the opinion of the authors, be used in conservation. *Recommended* materials showed no reactions at all. These recommendations are only true for silver containing photographic black-and-white prints.

Conclusion

The results of the accelerated aging test prove, that the selection of retouching and consolidation media is essential for photograph conservation treatments. Further examinations should be undertaken to define the suitability of a wider range of pigments and binding media.

Acknowledgement

This work was performed at the National Archives of Canada in partial fulfillment of the diploma, 'Identification, Conservation and Restoration of Coloured and Overpainted Photographs',¹⁴ at the Academy of Fine Arts in Vienna. The authors would like to thank both institutions for their support. Special thanks to the Picture Conservation Staff for valuable suggestions, encouragement, and assistance, especially Brian Thurgood and Joe Iraci from the Photograph Conservation Laboratory, John Grace and Greg Hill from the Paper Conservation Laboratory. The authors thank Gerhard Banik from the National Library of Austria and Werner Sobotka from the 'Höhere Graphische Bundeslehr- und Versuchsanstalt' in Vienna for their administrative support.

Literature

1. Hans Frank, *Vom Zauber alter Licht-Bilder*, Frühe Photographie in Österreich - 1840-1860 (The miracle of old photographs, early photography in Austria - 1840-1860) (Vienna: Fritz Molden, 1981) p. 102.
2. Adolf Krainer, "Geschichte der Bildnisphotographie und ihr Werdegang in Österreich" (History of portrait photography and its development in Austria), *Allgemeine Photographische Zeitung* Sondernummer '120 Jahre Photographie' (General photographic journal special edition '120 years photography') pp. 22-36 (Vienna, Julius Dressler, 1959), p. 28-29.
3. Fritz Kempe, *Daguerreotypie in Deutschland*, vom Charme der frühen Fotografie (Daguerreotypes in Germany, the charme of early photography) (Seebuck am Chiemsee: Heering, 1979), pp. 72, 74.

* This standard is now obsolete and was replaced by the ANSI IT 9.2.



Figure 11
Albin Mutterer: Miss Mutterer (1866);
during treatment, the right half of
the background cleaned from surface
dirt.



Figure 12
Albin Mutterer: Miss Mutterer (1866);
after treatment, in a new window
mat, keeping the original ensemble.

4. Conservation of Photographs, Kodak Publication F-40, (Rochester, N.Y.: Eastman Kodak Company, 1985) p. 126.
5. J. A. Barhydt, Crayon Portraiture (... complete instructions for making crayon portraits on crayon paper and on platinum, silver and bromide enlargements. Also directions for making french crystals.) (New York, N.Y.: The Baker & Tabor Co., 1892) p. 112.
6. Lothar Hentze, Practische und systematische Anleitung zur Portrait-Aquarell-Malerei, ihre Anwendung auf Photographien und alle Arten graphischer Abbildungen (incl. Landschaft), (practical and systematical instructions for portrait painting in watercolour, its application on photographs and all sorts of graphic figures (including landscape)) (Leipzig: M. Oelsner, 1889) pp. 192-193.
7. James Newman (Ed.), The Principles and Practice of Harmonious Colouring in Oil, Water, and Photographic Colours: especially as applied to photographs on paper, glass and silver-plate (by an artist-photographer) (London: James Newman, 1863) p. 35, appendix p. 4.
8. Klaus B. Hendriks, "Care of Black-and-White Photographic Prints", in CCI Notes 16/4, (Ottawa: Canadian Conservation Institute, 1986), p. 2.
9. Elizabeth Moffatt and Marilyn Laver, "Erasers and Related Dry Cleaning Materials" (Analytical Report ARS No. 1738, Ottawa: Canadian Conservation Institute, 1981), p. 6.
10. Carey M. Lea (Ed.), Newman's Manual of Harmonious Colouring as Applied to Photographs. (Philadelphia: Benerman & Wilson, 1866), footnotes 37, 40, 98.
11. Larry H. Feldman, "Discoloration of Black-and-White Photographic Prints", Journal of Applied Photographic Engineering, vol. 7, No. 1.
12. American National Standard Institute, ANSI PH 1.53 - 1986 American National Standard for photography (processing) - processed films, plates, and papers - filing enclosures and containers for storage, (New York, N. Y.: American National Standard Institute Inc. 1986), Photographic Activity Test p. 10-11.
13. Tables from:
Klaus B. Hendriks and Sebastian Dobrusskin, 'Some investigations into painted photographs', (Handout, AIC-Photographic Materials Group Meeting, Kansas City, Missouri, March 3rd 1989, Ottawa: National Archives of Canada, 1989).
14. Sebastian Dobrusskin, "Identifizierung, Konservierung und Restaurierung von bemalten und übermalten Photographien" (Identification, conservation and restoration of painted and overpainted photographs) (Diploma at the Academy of Fine Arts in Vienna, June 1989).

Table I

Recommendations for the tested Winsor & Newton Artists' Water Colours (R).

Colour:	Evaluation:	Reaction with:			Comment:
		SP	AP	Azo	
Cadmium Red	not recommended	■		■	bleaching of silver
Cadmium Yellow	not recommended	■			bleaching of silver
Cerulean Blue	adequate			■	discolouration of silver
Chinese White	recommended				no reaction detected
Chrome Deep	adequate			■	discolouration of silver
Cobalt Blue	not recommended			■	discolouration of silver
French Ultramarine	not recommended	■	■		bleaching of silver
Ivory Black	not recommended	■		■	discolouration of silver
Lamp Black	not recommended			■	discolouration of silver
Lemon Yellow Hue	adequate			■	discolouration of silver
Manganese Blue	recommended				no reaction detected
Oxide of Chromium	adequate			■	discolouration of silver
Prussian Blue	adequate			■	discolouration of silver
Raw Umber	recommended				no reaction detected
Venetian Red	recommended				no reaction detected
Vermillion	not recommended	■	■	■	bleaching of silver
Viridian	adequate			■	discolouration of silver

Table II

Recommendations for the tested Ilford Cibachrome Transparent Retouching Dyes (R)

Colour:	Evaluation:	Reaction with:			Comment:
		SP	AP	Azo	
Black	not recommended	■		■	bleaching of silver
Blue	recommended				no reaction detected
Cyan	adequate			■	bleaching of silver
Green	adequate			■	bleaching of silver
Magenta	adequate			■	bleaching of silver
Red	adequate			■	bleaching of silver
Yellow	adequate			■	bleaching of silver

Key:


SP: salted paper
AP: albumen paper
Azo: silver gelatin paper
□ no reaction
■ little reaction
■ strong reaction

Key:

SP: salted paper

AP: albumen paper

Azo: silver gelatin paper

 no reaction little reaction strong reaction**Table III**

Recommendations for the tested Eastman Kodak Dry Dye Retouching Colors (R)































Colour:	Evaluation:	Reaction with:			Comment:
		SP	AP	Azo	
Blue	adequate				bleaching of silver
Brown	adequate				bleaching of silver
Cyan	adequate				bleaching of silver
Green	adequate				bleaching of silver
Magenta	adequate				bleaching of silver
Neutral	not recommended				bleaching of silver
Orange	not recommended				bleaching of silver
Red	not recommended				bleaching of silver
Yellow	adequate				bleaching of silver

Table IV

Recommendations for the tested Marshall's Photo Oils (R)

Colour:	Evaluation:	Reaction with:			Comment:
		SP	AP	Azo	
Duolack (R)	not recommended				yellowing of medium bleaching of silver
Extender	not recommended				silvering out yellowing of medium
P. M. Solution (R)	not recommended				bleaching of silver silvering out
Cadmium Yellow	not recommended				yellowing of medium bleaching of silver
Cheek	adequate				silvering out
Chinese Blue	adequate				bleaching of medium silvering out
Lipstick Red	not recommended				very long drying time no reactions detected
Navy Blue	adequate				discolouration of silver
Titan White	not recommended				discolouration of silver
Tree Green	not recommended				bleaching of silver discolouration of silver

Materials List

Acryloid B-72 [ethyl-methacrylate copolymer], Röhm & Haas Canadian Head Office, Commercial Plastic, 2 Manse Road, West Hill, Ontario, M1E 3T9, Canada.

Artists' Watercolours [in tubes], Winsor & Newton Inc., 555 Winsor Drive, P.O. Box 1519, Secaucus, N.J., 07094-1519, USA.

Cellofas B-3500 [sodium carboxymethyl cellulose], Imperial Chemical Industries (GB).

Cobalt drier [Cat.No. 594-2], M. Grumbacher Inc., New York, N.Y., 10001, USA.

Dammar [Singapore Dammar], G. J. Nikolas & Co., Industrial Finishes, 2800 Washington Blvd., Bellwood, Illinois, 60104, USA.

ELVACE No. 1874 [Dispersion], TALAS, Division of Technical Library Service, 104 Fifth Avenue, New York, N.Y., 10011, USA.

Gelatin [granular, Type B, purified, 100 Bloom, CAS Reg. 900708], Fisher Scientific, P.O. Box 9200 Terminal, Ottawa, Ontario, K1G 4A9, Canada.

Gum arabic [Acacia, U.S.P.], J. T. Baker, Chemical Co., Phillipsburg, N.J., 08865, USA.

Ilford Cibachrome Retouching Colours, Ilford Ltd, West 70 Century Road, Paramus, N.J., 07652, USA.

Klucel G [hydroxy propylcellulose], Hercules, 300 Delaware Avenue, 6th Floor, Wilmington, D.E., 19899, USA, Phone: (302) 575-5700.

Kodak Dry Dye Retouching Colours, Kodak Canada Inc., 9977 McLaughlin Road, Brampton, Ontario, L6X 2M4, Canada.

Linseed oil [alkali refined linseed oil, OMV 0327], Winsor & Newton Inc., P.O. Box 1519, Secaucus, N.J., 07096-1519, USA.

Mars Plastic No. 52650 [PVC-Eraser], Staedtler, Nürnberg, FRG.

Marshall's Photo-pencils and Photo-Oil Colours [in Tubes], John G. Marshall Co., P.O. Box 649, Deerfield, IL, 60015, USA.














Table V

Recommendations for the tested Marshall's Photo Pencils (R)

Colour:	Evaluation:	Reaction with:			Comment:
		SP	AP	Azo	
Cadmium Yellow	recommended				no reactions detected
Cheek	recommended				no reactions detected
Lipstick Red	recommended				no reactions detected
Navy Blue	recommended				no reactions detected
Sky Blue	recommended				no reactions detected
Tree Green	recommended				no reactions detected

Table VI

Recommendation for the tested binding media.

Binding medium:	Evaluation:	Reaction with:			Comment:
		SP	AP	Azo	
Acryloid B-72 (R)	recommended				no reactions detected
Dammar	not recommended				discolouration of silver
Elvace 1874 (R)	adequate				bleaching of silver
Gelatin	recommended				no reactions detected
Gum arabic	adequate				yellowing of medium
Sodium carboxy methylcellulose	recommended				no reactions detected
Linseed oil (W&N)	not recommended				yellowing of medium bleaching of silver
Linseed oil (W&N) + not recommended					silvering out
Cobalt drier (Grumbacher)					yellowing of medium bleaching of silver
					silvering out

RESUME :

Les aristotypes sont les derniers procédés à noircissement direct qui ont été utilisés à grande échelle entre 1890 et 1930. Ils sont à la charnière entre les procédés du XIX^{ème} siècle (papiers salés et albuminés) et les papiers modernes. Annoncés comme des procédés permanents dès leur apparition, ils n'en ont pas moins montré leur fragilité. Cette recherche a été entreprise dans le but de mieux connaître l'origine de ces procédés et les problèmes spécifiques à leur conservation.

Après avoir établi une bibliographie historique et technique, des aristotypes ont été observés au M.E.T. afin d'étudier la morphologie du dépôt argentique et suivre son évolution lorsque l'image se dégrade.

MOTS CLES :

Aristotypes, P.O.P, analyse au M.E.T de l'image argentique.

LES ARISTOTYPES, 1^{ère} partie.

"Technologie, conservation et analyse au M.E.T. des premiers papiers photographiques industriels à émulsion"

LAVEDRINE Bertrand, FLIEDER Françoise,
CRCDG, 36 rue GEOFFROY SAINT HILAIRE, 75005 PARIS.

ETUDE BIBLIOGRAPHIQUE

On désignait par aristotypes les premiers papiers photographiques industriels au collodio-chlorure d'argent vendus sous ce nom, en 1884, par E. Liesegang. L'année suivante, le procédé au gélantino-chlorure d'argent est commercialisé et, par extension, la plupart des praticiens l'appellent aussi aristotype. Au début du siècle ce nom est remplacé par papier celloïdine (procédé au collodion) et papier citrate (procédé à la gélatine). De nombreux autres procédés font leur apparition à la même époque.

Après 1920, ces papiers à noircissement direct disparaissent progressivement pour plusieurs raisons. D'abord ces émulsions sont peu sensibles et le temps d'exposition peut être long par temps couvert ou en hiver. Enfin la miniaturisation des négatifs rend les tirages contacts difficilement observables.

LES ARISTOTYPES AU COLLODIO-CHLORURE D'ARGENT

L'utilisation d'une émulsion au collodio-chlorure d'argent pour préparer des papiers photographiques a été proposée pour la première fois en mars 1865 par M. Wharton Simpson (24). Peu de temps après, Geymet (9) publie une formule similaire d'émulsion au collodion. Il met à profit la mauvaise adhésion entre le support et le collodion pour préparer une image pelliculable que l'on peut transférer sur une plaque de verre afin de produire une diapositive.

Les premiers papiers à noircissement direct au collodion sont mis en vente en 1866 à Paris (papier leptographique) et en 1867 par M. J.B. Obernetter à Munich mais ils ne connaissent qu'un succès relativement modeste (10) (23).

Après 1880 la situation évolue. Des négatifs gélatino-argentiques sur plaque de verre sont fabriqués industriellement et livrés prêts à l'emploi. Un nouveau public s'adonne à la photographie et trouve dans les aristotypes un moyen facile de faire des tirages positifs; il n'est plus nécessaire de préparer son papier. Les sociétés Liesegang (Dusseldorf) et J.B. Obernetter (Munich) commercialisent avec succès les papiers aristotypiques en 1884. En France, la diffusion est beaucoup plus tardive que dans le reste du monde. L'exposition universelle de 1889 révèle au public français ces nouvelles émulsions, quelques années plus tard leur usage se généralise.

Les avantages offerts sont incontestables : facilité d'emploi et de traitement, grande sensibilité (environ deux fois plus que le papier albuminé) (8)(13), suivi de la qualité de fabrication, aspect brillant, finesse remarquable de l'épreuve (5). Enfin, comparé au papier albuminé qui se dégrade en moins de dix ans, les aristotypes apparaissent comme inaltérables (12).

Vers 1893, pour répondre aux exigences esthétiques de l'époque, de nouveaux papiers au collodion d'aspect mat font leur apparition. Par l'intermédiaire d'un virage on peut reproduire les tonalités douces des platinotypes (procédé à base de platine).

ARISTOTYPES A LA GELATINE

Mise au point par Abney vers 1882, la fabrication industrielle de ces papiers a débuté en Allemagne avec E. Obernetter (fils de J.B. Obernetter) en 1885 et Liesegang en 1886 (6). Elle suit de près celle des papiers au collodio-chlorure d'argent et doit remédier à deux inconvénients: enroulement du papier dans les bains de traitement (virage-fixage) et décollement de la couche collodion ou rayures au cours des manipulations (3).

Les papiers mats étaient obtenus par l'ajout d'amidon, de kieselghür (silice) ou de kaolin porphyrisé (13) (18) (21).

Les usines Lumière fabriquent, à partir de 1892, des papiers au gélatino-chlorure d'argent et les vendent sous le nom de "papier citrate " ou "papier aristo". Leur production annuelle est de 2100 km en 1905 .

En Angleterre la société Ilford fabrique, sur machine, des aristotypes à partir de 1891.

Les papiers aristotypiques au gélatino-chlorure d'argent seront d'un usage courant jusque dans les années 1940. Vers les années 1950, ils trouvent une utilisation scientifique pour l'enregistrement des particules ionisées.

En 1987 Kodak en produisait encore sous le nom de "Studio Proof Paper " (n° cat. 143 31 68) et depuis 1988 la société Guillemot** en commercialise à nouveau.

PROCEDES HYBRIDES

Aristotype auto-vireur (6) (17) (20) :

Inventés par Ashman et Offord, ces papiers ont la même structure que ceux décrits précédemment, mais ils contiennent en plus les sels nécessaires à leur virage, généralement des sels d'or ou de platine. L'opération de virage s'effectue d'elle-même dans un simple bain de fixage.

Ces papiers étaient au collodion ou à la gélatine.

Aristotype sans couche de sulfate de baryum :

Plusieurs sociétés (Lamy, Marion, Lumière) fabriquent, à la fin du XIXème siècle, ces aristotypes. L'émulsion à base de gélatine est directement couchée sur le papier. Ces épreuves peuvent être confondues, lors d'une identification, avec les papiers salés.

Aristotype à l'amidon ou à la gomme arabique :

La gélatine (ou le collodion) est remplacée par un mélange amidon-dextrine. La société Marion fabrique ces papiers à la fin du XIXème siècle. Ils sont barytés, d'aspect lisse ou granuleux, et mats.

Une communication faite à la Société Française de Photographie en 1904 préconise la gomme arabique comme liant pour remplacer l'amidon. Il ne semble pas que cette invention ait eu des répercussions industrielles (19).

Papier casoïdine :

C'est une émulsion à base de caséine mise au point par Otto Buss en Suisse (1903) et fabriquée par O.Wilde à Goerlitz (Allemagne) puis par Gevaert à Anvers en 1905 (23).

Papier au chromate d'argent :

En 1898 Ferdinand Hrdlicka (Vienne) dépose un brevet pour un nouveau papier, adapté aux négatifs "faibles". Cette nouvelle émulsion au collodion contient du chromate d'argent, elle est vendue sous le nom de papier "Rembrandt" (6) (23).

Papier au protalbine :

Inventé par Jolles et Léon Lilienfeld en 1897 à Vienne, ce papier est commercialisé avant 1900 par la Wiener Chemische Werke et Protalbin Werke (Dresden). Le liant est préparé à partir d'une solution alcoolique de protides extraits de graines de céréales; il peut être mélangé avec de l'albumine, du collodion ou de la gélatine (brevet DRP Nr 99652, Dr Jolles, Lilienfeld & Co, Wien) (6) (23).

LA FABRICATION INDUSTRIELLE

La mécanisation de la fabrication, qui n'a jamais pu être envisagée pour des papiers albuminés, va permettre une production à grande échelle. Les premières machines avaient à l'origine une structure assez simple et demandaient sans doute un faible investissement, d'où l'extraordinaire essor de petites compagnies qui fabriquaient des papiers aristotypiques au début du siècle. Le premier couchage industriel est réalisé par A. Kurtz sur des machines à cylindre (23).

Une des caractéristiques de ces premiers papiers industriels est la nature de leur support.

Avant de recevoir l'émulsion photosensible, le papier fait l'objet d'une préparation préalable: le barytage. Cette méthode, proposée dans un brevet en 1881 par Hutinet et Lamy (11) et destinée, à l'origine, à produire une épreuve photographique d'aspect brillant, consiste à enduire le papier d'une couche de sulfate de baryum (parfois d'oxyde de zinc) en suspension dans une solution de gélatine, de gomme arabique ou d'albumine. La gélatine est le liant le plus fréquemment utilisé.

Le barytage marque un pas important dans l'évolution des techniques. Il permet d'améliorer les qualités physiques, optiques et chimiques du support.

TRAITEMENT DES ARISTOTYPES

Tirage :

Le papier, placé sous le négatif, est maintenu en contact pendant l'insolation qui peut durer de quelques minutes à plusieurs heures selon la densité du négatif et l'intensité de la lumière du jour. Les parties exposées à la lumière noircissent, l'image apparaît de plus en plus intense et prend une tonalité rouge brique à violet. Ce noircissement rapide à la lumière est dû à la composition chimique ; l'émulsion contient du nitrate d'argent en excès.

Plusieurs chercheurs avancèrent des théories pour expliquer la formation de l'image. En 1849, E. Becquerel (2) imagine un mécanisme qui trouve un large écho dans le milieu scientifique et est repris par différents auteurs pendant plus de cinquante ans. D'après cette théorie, il se forme à la lumière une espèce chimique appelée "sous-chlorure d'argent" (Ag_2Cl ou Ag_4Cl_3) selon le processus suivant (13):



D'autres scientifiques, dont Davanne et Girard dès 1855, puis Lumière (4) et Lüppo Cramer (22) rejettent cette théorie et pensent qu'il se forme non pas un sous-chlorure d'argent mais un complexe argent colloïdal-chlorure d'argent [Ag-AgCl].

Le développement de nouvelles méthodes d'analyse comme la diffraction de rayons X mettra une fin décisive vers 1930 à la théorie des sous-chlorures en montrant que l'action de la lumière provoque l'apparition d'une seule espèce chimique qui est l'argent sous forme colloïdale.

La couleur de l'image est due à la finesse des particules d'argent. Les particules les plus petites absorbent les faibles longueurs d'ondes; plus leur taille augmente, plus l'absorption s'élargit et se déplace dans le sens des longueurs d'ondes croissantes.

Virage et fixage :

L'opération de virage avait initialement un but esthétique. Il existe de très nombreuses formules de virage donnant les teintes les plus variées. Les bains de virage à l'or et au platine étaient les plus couramment employés. Le métal déposé modifie les caractéristiques chimiques et physiques des grains d'argent, leur taille et leur forme évoluent. La couleur de l'épreuve variera selon la formule, la dilution, le temps d'immersion, la température...

Après 1914, le prix de ces métaux précieux n'a cessé d'augmenter. Les photographes ont cherché à les remplacer par des composés moins onéreux et capables de produire des résultats visuels satisfaisants. Les sels de plomb procurent des tons violets très acceptables mais la permanence de l'épreuve est réduite. Le plomb est donc à proscrire des bains de virage sauf s'il est utilisé avec des sels d'or (15). Seul le virage au sélénium permet d'allier des tonalités agréables et un prix abordable tout en garantissant une conservation à long terme (16).

Fixage :

Le bain de fixage élimine les sels d'argent sensibles non utilisés. Lors de l'immersion de l'épreuve on constate un affaiblissement et un changement de tonalité. Ces deux phénomènes, qui ne se produisent pas avec les papiers à développement, ont plusieurs origines physiques et chimiques.



PHOTO N°1
OBSERVATION AU M.E.T. D'UNE
COUPE TRANSVERSALE D'UN
TIRAGE ANCIEN SUR PAPIER
ALBUMINE (10000 X)

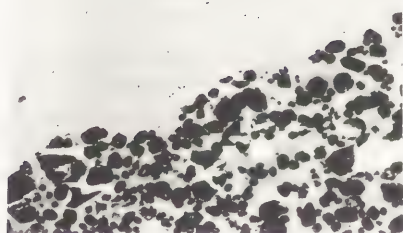


PHOTO N°2
OBSERVATION AU M.E.T. D'UNE
COUPE TRANSVERSALE D'UN
ARISTOTYPE MODERNE A LA
GELATINE (10000 X)



PHOTO N°3
OBSERVATION AU M.E.T. D'UNE
COUPE TRANSVERSALE D'UN
ARISTOTYPE AU COLLODION
(45000 X)

Bain de virage-fixage combinés :

Un bain de virage-fixage permet de réaliser simultanément les deux opérations. Le fixateur contient des sels d'or. Si l'utilisation d'un bain unique simplifie les manipulations, certains auteurs le suspectent d'être la cause d'altérations (1) (5). Lumière et Seyewetz ont montré qu'il n'en n'était rien (14) (15). Leurs travaux révèlent que le facteur principal de la dégradation des images est la présence d'hyposulfite non éliminé lors du lavage.

ETUDE EXPERIMENTALE, ANALYSE AU M.E.T.

PREPARATION DES ECHANTILLONS

Papier photosensible :

Nous avons, dans un premier temps, limité notre expérimentation aux procédés les plus répandus: les aristotypes à la gélatine et les aristotypes au collodion. La technique de couchage retenue consiste à transformer une feuille de papier baryté (24x30cm) en cuvette, en pliant les bords sur une hauteur de deux à trois centimètres. L'émulsion photosensible est alors versée dans cette cuvette et répandue uniformément sur le fond par oscillation. Après le séchage en chambre noire, la feuille est mise à plat, les bords sont découpés de façon à ne conserver que le fond de la cuvette. Le papier est alors utilisé pour le tirage. Ce mode opératoire a été appliqué pour les émulsions au collodion. Pour les émulsions à la gélatine, nous avons employé le papier citrate Guillemot (aristotype à la gélatine).

Tirage :

Le papier est exposé, dans un châssis-presse, sous une lampe au xénon ou une lampe à vapeur de mercure. Le négatif utilisé pour le tirage est une gamme de gris présentant une douzaine de plages homogènes de densités croissantes. Ensuite, le papier est éventuellement viré à l'or, puis fixé et enfin lavé à l'eau courante.

ANALYSE DES ECHANTILLONS

Les mesures de densité optique nous révèlent que, d'un échantillon à l'autre, on peut observer d'importantes différences de densité selon que le bain de fixage est acide ou basique. Ces résultats confirment des travaux antérieurs comme ceux de Formstecher (7), en apportant certaines précisions: le fixage en milieu acide provoque effectivement une perte de densité quand le tirage a été viré à l'or (courbes n°1). Si la photographie n'a pas été virée, la perte de densité est limitée aux zones de faible densité; dans les parties denses, on obtient, au contraire, des densités supérieures (courbes n°2). Ces observations nous conduisent à employer un bain de fixage acidifié s'il n'est pas précédé d'un virage à l'or (comme le montrent les courbes sensitométriques, la gamme des valeurs de densité sera beaucoup plus étendue). Au contraire, un virage à l'or sera suivi d'un fixage en milieu basique.

Analyse au M.E.T.:

La perte de densité et le changement de couleur que peuvent présenter ces images ne font que traduire une modification de la morphologie du dépôt argentique. Afin de mieux suivre ce phénomène nous avons décidé d'observer la structure du dépôt argentique. La taille des particules d'argent étant de l'ordre d'une dizaine de nanomètres, il faut travailler avec un Microscope Electronique à Transmission (M.E.T.). Dans ce but nous avons inclus des prélèvements effectués sur des aristotypes dans des blocs de résine. Ils ont été découpés ensuite sur un ultra-microtome et nous avons observé ces coupes au M.E.T.

Résultats préliminaires :

L'observation au microscope électronique à transmission (photo n°2, 10000X)* révèle immédiatement deux éléments caractéristiques. Les grains de sulfate de baryum sont parfaitement visibles dans la partie inférieure droite de la photographie. Les grains d'argent de la photographie sont uniformément répartis dans la couche; ceci montre que la feuille n'a pas été trempée dans un bain sensibilisateur comme c'est le cas des

papiers à l'albumine(photo n°1, 10000X), mais recouverte d'une émulsion phototosensible où les cristaux d'halogénure d'argent sont dispersés de façon homogène.

La comparaison entre la photographie n°1 et n°2 met en évidence ces différences.

Nous avons ensuite comparé les coupes faites sur des aristotypes au collodion avec celles faites sur des aristotypes à la gélatine. Ces prélèvements ont été réalisés dans des zones de haute densité. En comparant les observations faites au M.E.T., on constate que la taille des particules varie énormément (photo n°3, 4, 5, 45000X).

Du point de vue théorique ceci peut provenir des techniques de préparation: les composés utilisés pour chacune des émulsions ne sont pas les mêmes et le mode opératoire (température, agitation, vitesse d'addition des composés...) est reconnu depuis longtemps comme un facteur déterminant pour la taille des cristaux d'halogénures. Afin de ne pas multiplier les paramètres, nous avons utilisé, dans un premier temps, toujours le même type de papier. Le papier citrate Guilleminot** offre une régularité de fabrication que seul peut assurer un couchage industriel.

Nous avons alors effectué des prélèvements à des endroits correspondant à des densités différentes. Dans les zones de faible densité (photo n°6, 45000X), le nombre et la taille des grains sont moins importants que dans les zones de forte densité (photo n°7, 45000X).

Ces observations quant à la répartition et à la taille des grains doivent être accompagnées d'une mesure quantitative. Etant donné la disparité de la taille des particules, seule une étude statistique de leur répartition peut nous permettre d'apprécier valablement un changement apparu au cours du traitement. Ces études statistiques sont d'ailleurs appliquées par les fabricants d'émulsion pour évaluer la taille des cristaux d'halogénure d'argent. La courbe de fréquence est tracée à partir du comptage de 1000 particules. Toute modification dans la répartition se traduit par un changement d'allure de cette courbe.

Pour rendre les mesures plus précises et moins fastidieuses, nous avons décidé d'effectuer un traitement numérique de l'image. Des clichés pris au M.E.T. sont numérisés, l'image est ensuite traitée et analysée en morphologie mathématique. Dans ce but nous utiliserons le logiciel Optilab^R développé par la société Graftek***. Pour chaque particule analysée ce logiciel donne une quarantaine de paramètres dont la taille, le périmètre, le facteur de circularité, le facteur de compacité etc... Cette étude se poursuit actuellement.

CONCLUSION :

L'analyse des aristotypes au M.E.T. s'est révélée tout à fait intéressante. Si le traitement numérique des images obtenues au M.E.T. s'avère efficace, nous aurons établi une procédure rapide que nous nous proposons d'appliquer pour suivre l'évolution de la morphologie du grain d'argent au cours du virage, des vieillissements accélérés et éventuellement des traitements de restauration. Ce type d'analyse doit pouvoir être étendu aux amas de filaments des photographiques développées. En effet les prodigieuses possibilités qui sont offertes par la micro informatique et ce type de logiciel permettent de paramétrer des structures de formes très variées.

*Les photos au M.E.T.(PHILIPS EM 201, 80kV) ont été faites au Service d'Accueil de Microscopie Electronique, CNRS, Université de Paris VI, 105 Bd Raspail, 75006 Paris.

**Guilleminot, 22 rue de Chateaudun, 75009 Paris tél. 42 80 65 80.

*** Graftek, 9 route de Verrières, 92360 Meudon la Forêt tél. 46 31 24 24.

PHOTO N°4
OBSERVATION AU M.E.T. D'UNE
COUPE TRANSVERSALE D'UN
ARISTOTYPE A LA GELATINE
(45000 X)

PHOTO N°5
OBSERVATION AU M.E.T. D'UNE
COUPE TRANSVERSALE D'UN
ARISTOTYPE A LA GELATINE
(45000 X)

PHOTO N°6
OBSERVATION AU M.E.T. D'UNE
COUPE TRANSVERSALE D'UN
ARISTOTYPE A LA GELATINE,
D=0,18 (45000 X)



PHOTO N°7
OBSERVATION AU M.E.T. D'UNE
COUPE TRANSVERSALE D'UN
ARISTOTYPE A LA GELATINE,
D=1,86 (45000 X)

REFERENCES

- (1)BAKER (H.), "The permanency of matt collodion paper", British Journal of Photography, 1905, 10 novembre, pp. 897-898.
- (2)BECQUEREL (E.), Annales de Physique. et Chimie, 3e série, 22, 1848, p. 332.
- (3)CAMPO (O.), "Procédé d'impression pour positive sur papier gélatino-chlorure (procédé dit Aristotype)", Bulletin de la Société Française de Photographie, 1888, pp. 271-275.
- (4)DAVANNE (A.), La photographie, Paris, Librairie Gauthier-Villars, 1886 Reprint, New-York, ArnoPress, 1979.
- (5)DECK (N.C.), "Stability of photographic prints", Bulletin de la Société Française de Photographie, 12, 1925, pp. 384-385.
- (6)EDER (J.M.) ,WENTZEL (Fritz), Handbuch der Photographie, Handbuch, 1928, vol. IV, part I.
- (7)FORMSTECHE (F.), "The alkaline fixing bath in the printing out process", Photographische Industrie, 1924, p. 855.
- (8)GELDMACHER (F.W.), "Collodio chloride printing by an improved method", British Journal of Photography, 5 février 1886, pp. 83-84.
- (9)GEYMET (), "Note", Bulletin de la Société Française de Photographie, 1865, pp. 176-178.
- (10)HANNEKE (P.), Das Celloïdin Papier, Berlin, Verlag von Gustav Schmidt, 1897.
- (11)HUTINET et LAMY, "Procédé de préparation d'un papier photo gélatino-bromuré, chloruré, ioduré en vue d'obtenir des épreuves brillantes", Brevet n° 142141 du 5 avril 1881.
- (12)LIESEGANG (P.E.), "L'aristotypie ou le tirage au collodio-chlorure d'argent ", Le moniteur de la photographie, 1885, pp. 124-125.
- (13)LUMIERE (A.) et FILS, "Procédé pour l'obtention d'émulsion photographique donnant des couches mates", Brevet n° 296478 du 20 janvier 1900.
- (14)LUMIERE (A.) et (L), SEYEWETZ (L.), "Sur l'altération des épreuves positives imprimées sur papier au chlorocitrate d'argent et virées et fixées en une seule opération", Bulletin de la Société Française de Photographie, 1902, pp. 409-417.
- (15)LUMIERE (A.) et SEYEWETZ (L.), "Sur l'altération des images imprimées sur papier au chlorocitrate d'argent et fixées en une seule opération", Bulletin de la Société Française de Photographie, 1908, pp. 481-483.
- (16)LUMIERE (A.) et SEYEWETZ (L.), "Sur l'emploi du sélénium comme succédané dans les virages des papiers à noircissement direct.", Bulletin de la Société Française de Photographie, 1924, pp. 79-80.
- (17) LUND (P.), "Papier autovireur", Bulletin de la Société Française de Photographie, 1900, p. 334.
- (18)MATHET (L.), Dictionnaire de chimie photographique, 2ème édition, Paris : Charles Mendel Editeur, 1901.
- (19)REISS (), "Préparation d'un papier à la gomme arabique et au nitrate d'argent", Bulletin de la Société Française de photographie, 1904, pp. 521-526.

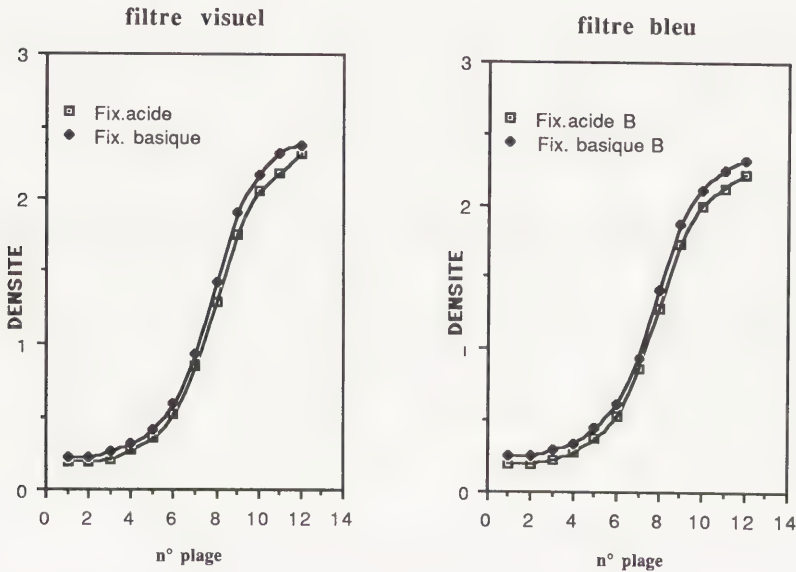
(20)SALMON (P.R.),"The modern history and manipulation of self-toning papers", British Journal of Photography, 1921, 9 décembre, pp. 730-733.

(21)SWAN (A.), "Photographic print collection", Library Trends : conservation of library materials, 30, n° 2, 1981, pp. 267-296.

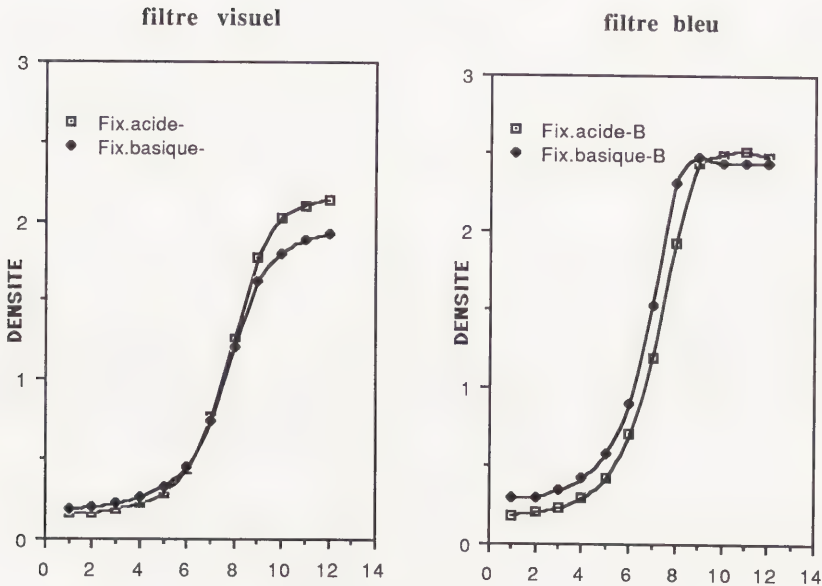
(22)VASSY (A.),Fondements théoriques de la photographie, Paris : Edition de la Revue d'Optique, 1953.

(23)WENTZEL (F.),Memoirs of a photochemist, Philadelphie : L.W. Sipley editor , 1960.

(24)WHARTON (S.),"Sur une nouvelle méthode de tirage et sur la préparation et l'emploi du collodio-chlorure d'argent", Bulletin de la Société Française de Photographie, 1865, pp. 151-157.



Courbes n°1:
Comparaison des effets d'un fixage acide avec ceux d'un fixage basique.



Courbes n° 2 :
Comparaison des effets d'un virage à l'or suivi soit d'un fixage acide soit d'un fixage basique.

ABSTRACT:

The multilayer structure of tintype photographs and the interaction between these layers was examined. Scanning electron micrographs of fractured tintype coatings revealed the typical thickness and interface locations for the iron plate substrate, japanned coating, collodion, silver image particles, and overcoat varnish. Fracture pattern stress lines traversing the different polymer regions verified that a discrete collodion-japan interface exists while a less distinct transition appears between overcoat varnish and the collodion-silver region. Additionally, image flaking typically associated with corrosion of the iron substrate was found to occur as grain-boundary separation within the iron plate rather than adhesion failure of the organic coatings at the iron-japan layer interface. The ability to distinguish the various coating layers and the silver particle matrix on the basis of SEM image features was corroborated by energy dispersive spectroscopy (EDS).

KEYWORDS

tintype, collodion, ambrotype, cellulose nitrate, ferrotype, wet plate

The Multilayer Structure of Tintypes

Mark H. McCormick-Goodhart
Conservation Analytical Laboratory
Smithsonian Institution
Washington DC, 20560

INTRODUCTION

Tintypes are wonderful examples of the Collodion Era of photography. Their simple virtues endeared them to the public from the late 1850s well into the 1880s and early 90s. The advent of the tintype provided a new substrate for the photographer, not a new imaging process. In fact, the collodion process, having been disclosed to the world freely in 1851 by F.S. Archer^{1,2}, did not require any modification in order to accommodate the new substrate, and the labor intensive act of cleaning glass substrates was avoided altogether with tintypes. Photographers were able to charge a lower price for tintypes primarily because the japanned surface was able to receive the collodion coating with no make-ready effort other than perhaps dusting with a camel's hair brush. Thus, tintypes share a generic collodion coating, sensitizing, and processing procedure along with ambrotypes and "wet plate" negatives, but were still easier to make because of the substrate handling properties. A cross-sectional analysis should reveal the following layers: an iron plate, the japan coating, a collodion binder with silver particles representing processed image, and finally, a varnish overcoat layer. These layers cannot be viewed simultaneously at a single magnification with sufficient detail, however, since the collodion binder with silver matrix is an exceptionally thin region compared to the other layers.

EXPERIMENTAL:

Scanning electron microscopy was chosen as a research tool because the fine multilayer structure of collodion artifacts is not easily seen by conventional light microscopy techniques. The calculated thickness of the collodion binder reinforced this premise. By converting typical 19th century collodion recipes to metric equivalents it was found that successful wet collodion photography works in a relatively narrow parameter space. Table 1 illustrates the metric conversion of formulas compiled by Towler for his photographic manual, *The Silver Sunbeam*.³ Coating experiments with these formulas and according to the hand crafted methods of the Collodion Era demonstrated that 3 to 5 ml. of collodion is retained on a 10 x 12.5 cm. plate after the excess is drained according to the customary practice. Given that Ommeganck's recipe, for example, called for 9 grams per liter of pyroxylin (cellulose nitrate) and will cover a 125 sq. cm. plate with a 5 ml. wet volume, and taking the specific density of pyroxylin at 1.66 grams per cc., the dry thickness of the collodion binder may be estimated:

$$9 \text{ gm/l} \times 1 \text{ l}/1000\text{ml} \times 5 \text{ ml}/125\text{cm}^2 \times 1\text{cm}^3/1.66 \text{ gm.} = t, \text{ the coating thickness.}$$

Solving for t , the thickness is 2.17×10^{-4} cm., approximately 2 microns.

The identification of coating interfaces by SEM image topography rather than elemental mapping would require that surface marks unique to the various coatings be distinguishable. Sample preparation by means of embedding, cross-sectioning, and polishing might obliterate such features. Furthermore, the solvent systems of various embedding materials might swell or distort the tintype coatings. With these concerns in mind the decision was made to experiment with simple fracturing techniques. Clean cross-sectional faces were prepared by bending small sections of substrate sharply in the direction away from the image layer and then removing coating fragments using a dissecting needle while observing under a 50x power stereoscope. Inexpensive tintype samples were purchased for this experimental work from various dealers at recent local antique photo shows. They were of unidentified sitters and chosen with regard to color, density, and overall appearance from the standpoint of being highly representative examples of the craft. Some were also acquired because they exhibited common deterioration signs such as cracks, blistered coatings, corroded iron surfaces, etc., while other samples were technically in excellent condition.



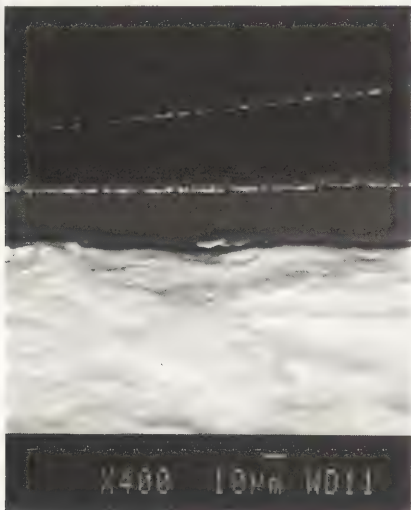


Figure 1. Topography of the tintype's organic coatings on the iron substrate. Bright rows of particles are image silver. 4μ varnish coating edge is just noticeable above the silver particles. Leveling properties of the japan layer can be easily seen.

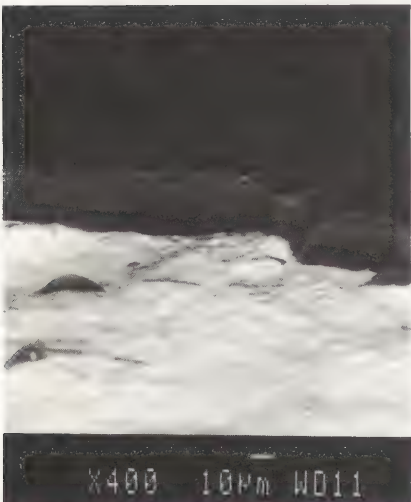


Figure 2. Same perspective as fig. 1 except that few silver particles show because a shadow area (low density silver region) of the tintype picture is shown.

Iodized Collodion Formulas			
	#1	#2	#3
Alcohol	660 ml	304 ml	470 ml
Ether	340 ml	693 ml	530 ml
pyroxylin	10.9 g	9.0 g	7.6 g
Ammonium Iodide		4.5 g	3.8 g
Ammonium Bromide			0.7 g
Lithium Iodide	4.4 g		
Cadmium Iodide	4.4 g	4.5 g	3.8 g
Cadmium Bromide	1.5 g	2.3 g	0.8 g
Iodine	optional		0.4 g

Table I. Iodized Collodion recipes of Towler (#1), Ommeganck (#2), and Disderi (#3). Note the variations in ether/alcohol ratios while maintaining a low overall pyroxylin content.

RESULTS:

Figures 1 and 2 show the overall topography of the iron sheet and the surface leveling characteristics of the japan layer. The well ordered matrix of silver grains in a highlight region of the plate (high density silver region) shows distinctly in figure 1 while in figure 2 a deep shadow area from the same tintype demonstrates that few silver particles were developed there. Adhesion failure for this tintype sample was consistently at the iron-japan interface. No iron corrosion evidence was noted. The 5 micron overcoat varnish is just noticeable at 400x in these photos. A primary function of the overcoat varnish can be seen in Figure 3. A scratch traverses the varnish surface but does not reach the silver particles approximately 4 microns underneath. The collodion binder layer location is marked by the fine row of silver particles, but its boundaries are not distinct at 800x magnification. The japanned layer is 40 microns thick and has torn away from the iron plate taking several microns of iron (or iron-base oxides) with it. This interesting fact can be more clearly shown by the perspective provided in Figure 4. Figure 5 is the same view except that a backscattered electron image was acquired compared to the secondary electron image in figure 4. The backscattered electron image dramatically enhances the location of the silver grains. Figures 3-5 all document a tintype sample that exhibited one corrosion related defect in the picture when purchased. This tintype had a 1 cm. diameter coating blister, but otherwise most of the image surface appeared to be completely intact. The SEM sample was taken from a portion of the plate that was not blistered. Yet when fractured during preparation it became immediately apparent that iron corrosion was occurring to some degree over the entire substrate. Clearly, once the iron corrosion is initiated, an intergranular fracture takes place within the iron plate to produce image loss in preference to an organic coating adhesion failure.

Figure 6 is perhaps the most revealing micrograph of all. At a magnification of 6000x differential stress lines in the three organic layers of varnish, collodion, and japan coating, can be used to interpret the location of their boundaries. The silver particles do not form a densely clustered matrix because the sample location is not a highlight image area. Additionally, no distinct varnish-collodion interface is present. Careful examination of the stress line orientation strongly suggests that varnish liberally penetrated the image silver matrix which was not deeply embedded in the collodion binder. The processed silver grains reside in the upper portion of the collodion with much grain surface area exposed before a varnish overcoat encapsulates them. The close solubility parameters of the typical spirit varnishes and the collodion binder may also help to explain why the varnish-collodion-silver region behaves more as a transitional region than a discrete boundary. The collodion binder just underneath the silver matrix has a different stress pattern orientation which visibly differentiates it from both the overcoat varnish layer above and the japanned surface below. It measures approximately 2 microns thick which is in excellent agreement with the value predicted by the experimental coating

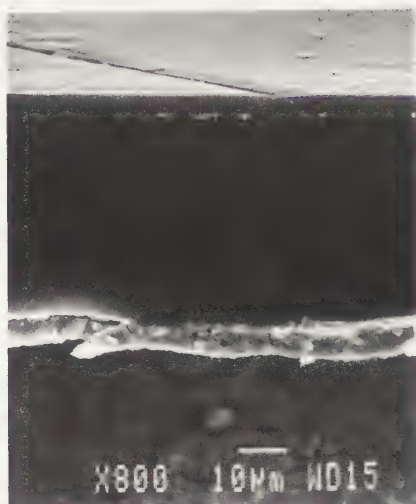


Figure 3. From top to bottom of photo: 1). Varnish surface with transverse scratch in view; 2). 4μ varnish region; 3). Silver particles, but undetectable collodion thickness; 4). 40μ japanned coating; 5). Iron/iron oxides several microns thick adhering to japan coating. 6). Iron substrate, separated from coatings and out of focus.

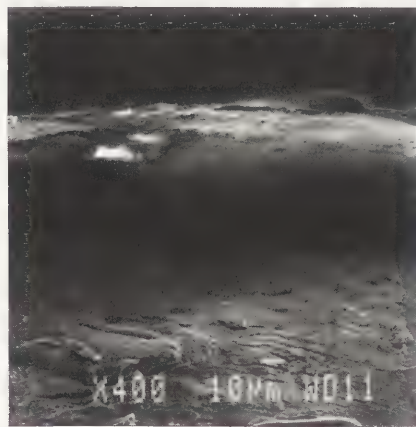


Figure 4. Secondary electron image showing perspective of grain-boundary separation of the iron support.

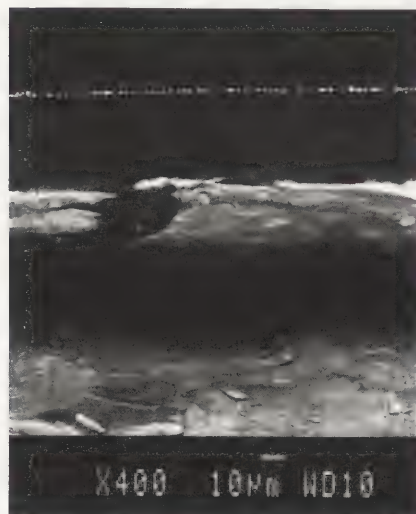


Figure 5. Backscattered electron image, same view as figure 4.

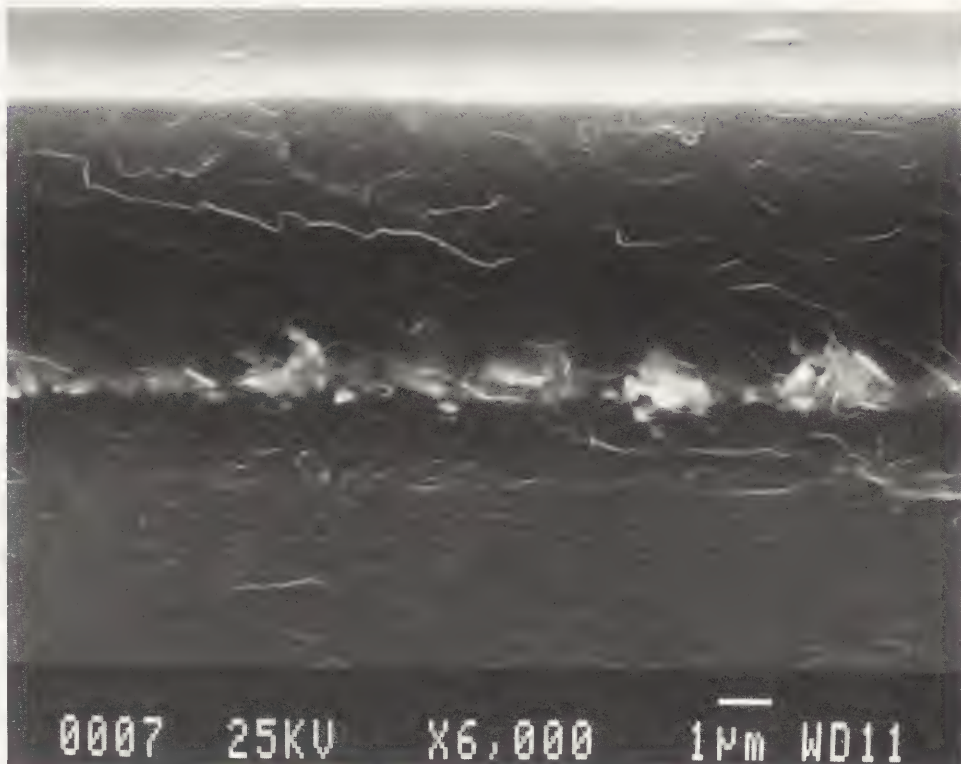


Figure 6. Detailed cross-sectional view of a tintype's coating structure. From top to bottom in photo: 1) Surface edge of varnish; 2). 5μ thick varnish layer exhibiting strong diagonal fracture lines; 3). 1μ thick matrix of embedded silver particles; 4). 2μ thick collodion; 5). Japanned layer region. A sharp change in the fracture pattern stress line orientation marks the collodion-japan interface.

data. Unlike the overcoat varnish, the japanned surface was an oil varnish rather than a spirit varnish. For an oil varnish, drying or more correctly hardening takes place by polymerization rather than solvent evaporation. The polymerization may be thermally initiated, and in fact ferrotype manufacturers brushed on the japan coating, allowed it to level, and then baked the product in an oven to create the hardened finish. Figure 6 also shows that the collodion-japan interface is a sharply defined boundary. The ether and alcohol of the wet collodion process did not attack the japanned surface to any appreciable extent. An excellent bond was noted in all samples, and once again, fractured samples did not show any delamination at the japan-collodion interface or in the spirit varnish-silver-collodion region.

Compositional analysis by energy-dispersive spectroscopy (EDS) was carried out to confirm that these materials were in the location they appeared to be. Analysis was performed after identification had tentatively been made for each apparent region based on the visual data. The results are shown in figures 7-11. Organic components are, of course, undetected by EDS, but inorganic impurities were anticipated that would give a distinct signature for the various organic layers, and this turned out to be the case. The varnish overcoat, for example, exhibits a high percentage of chlorine (figure 7). Although external sources such as contamination by fingerprints or ocean salt spray might serve to explain the chlorine presence, the author believes that this varnish contains some portion of bleached shellac resin. The use of bleached shellac, also referred to as white lac, was very common. An article appearing in the *British Journal of Photography* in 1877 entitled "Shellac, and its use in varnishes" stated, "Bleached lac has for a long time been a favourite, and, indeed, the leading basis in the published formulae for photographic varnishes..."⁴ Decolorizing shellac by first hydrolyzing the resin in an alkali solution, introducing sodium hypochlorite to remove the color, and then precipitating the resin out of solution by addition of acid was well known and practiced. Residual chlorine would undoubtedly be present to some extent in a bleached lac. Next, the silver grain analysis (figure 8) correctly displays a strong silver peak. The author believes that the copper and zinc signal is an artifact of the detector and sample mounting geometry rather than actual impurities associated with the silver. A single silver grain could not be isolated entirely so the presence of chlorine in the silver grain analysis is reasonably taken to be from the surrounding varnish material. Similarly, the collodion binder displays a mixture

of impurities derived from the other constituents, but repeated analyses at different locations verified the consistently identifiable profile for the collodion region as per figure 9. The japan layer, found to vary between 25 and 40 microns thick, is shown in figure 10. The analysis was carried out at approximately the center of the cross-sectioned layer. Note that no chlorine was detected indicating that the japan layer significantly isolated chlorine from the iron plate. However, due to the detection limits it cannot be concluded that the isolation is 100% effective. Trace levels of chlorine might still be available to accelerate iron plate corrosion. Finally, figure 11 confirms the iron support. The analysis was of the surface after the japan layer had been flaked off. The low level of sulfur in the data is most likely surface residue from the japan layer rather than a compositional percentage of the iron support. No detectable impurities would be expected in the iron support because the U.S. ferrotype manufacturers used a high quality sheet iron denominated "charcoal iron" which was imported from England.⁵ Charcoal iron refers to the use of a more expensive fuel, charcoal, rather than coal in the furnace when the iron was smelted or refined in order to control the impurities, especially sulfur. Such iron products can be virtually free of sulfur to levels below any available detection methods. The level detected here would be an enormous impurity in the iron process if it actually represented the bulk composition.

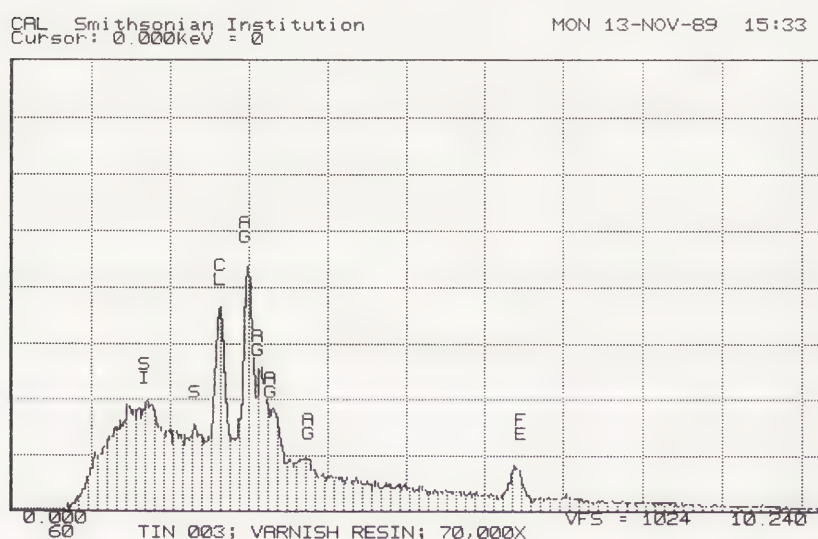


Figure 7. EDS data for Varnish overcoat. Note chlorine and sulfur peaks.

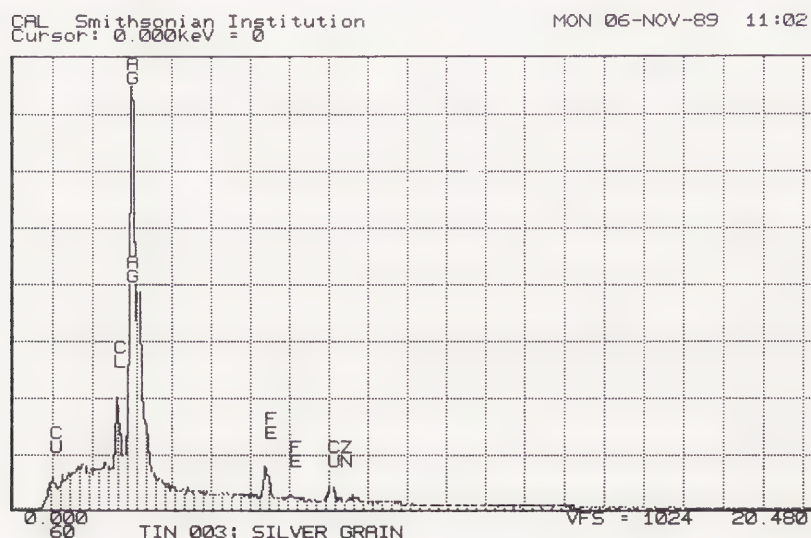


Figure 8. Silver grain analysis by EDS.

CAL Smithsonian Institution
Cursor: 0.000keV = 0

MON 13-NOV-89 15:45

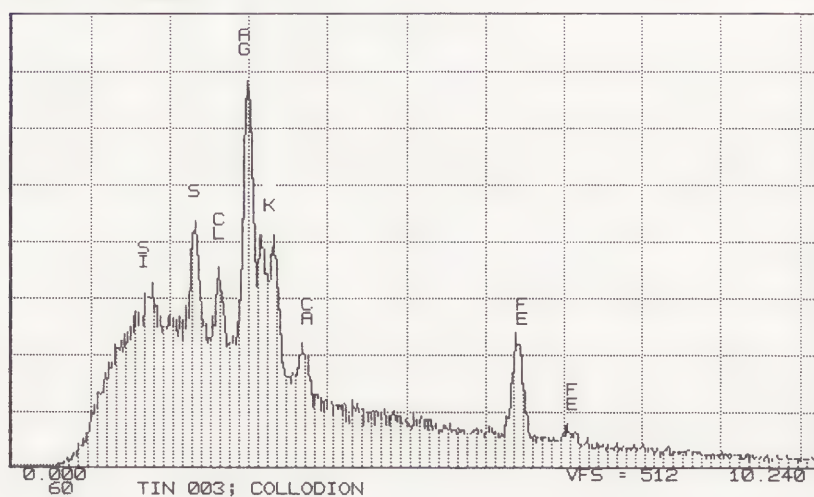


Figure 9. Collodion "signature" by EDS. Compare chlorine and sulfur peaks to varnish overcoat (figure 7).

CAL Smithsonian Institution
Cursor: 0.000keV = 0

MON 13-NOV-89 15:41

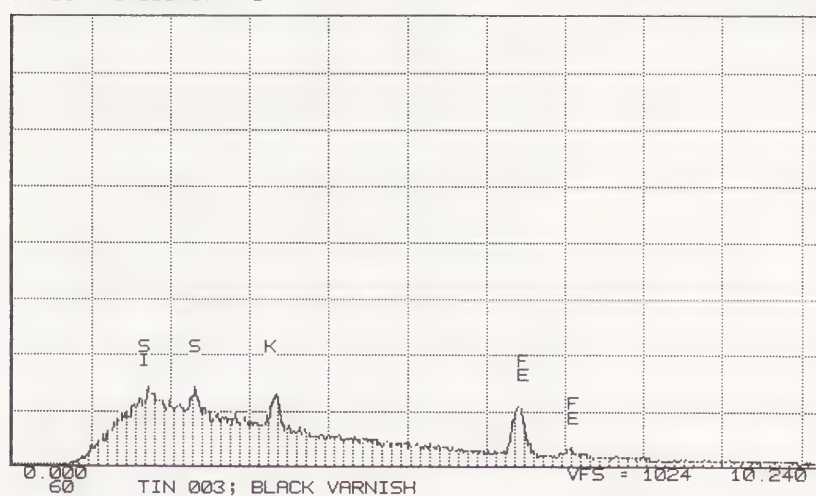


Figure 10. EDS data for japanned layer.

CAL Smithsonian Institution
Cursor: 0.000keV = 0

MON 06-NOV-89 10:55

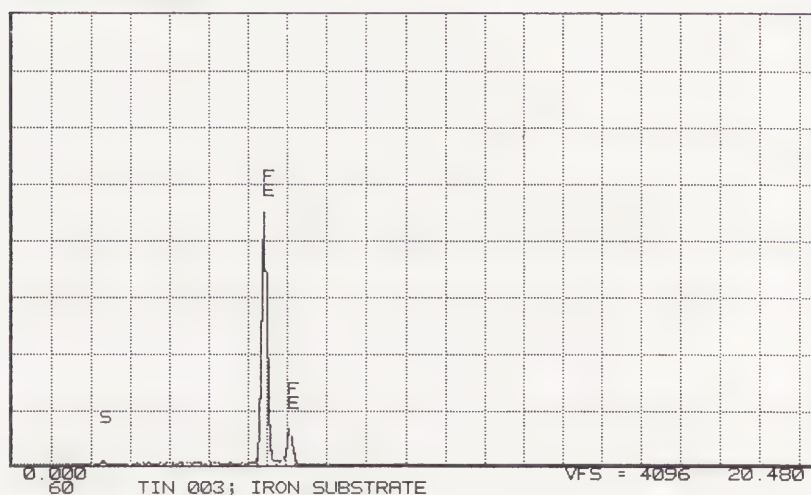


Figure 11. EDS data for iron substrate surface after japanned layer removed. Detected sulfur is residue from japanned coating.

CONCLUSIONS:

Typical coating layer thicknesses for tintypes were found to be of the following order:

- 1). Varnish overcoat; 4 to 8 microns.
- 2). Silver matrix; 1 micron, located at top of collodion binder.
- 3). Collodion; 1 to 2 microns.
- 4). Japanned coating; 25 to 40 microns.

Iron corrosion endangers the image layer by leading to grain-boundary separation within the iron support as opposed to coating adhesion failure at the japan-iron/iron oxide interface. This explains why severe "blistering" of the coatings is often seen on tintypes before adhesion failure ultimately occurs. At a less advanced stage iron corrosion in progress is masked by the organic coatings comprising the tintype image.

Spirit varnishes which were used by the photographer to protect the silver image from chemical and mechanical damage as well as to impart aesthetic qualities were frequently dissolved in an alcohol containing solvent system. This promoted varnish penetration into the collodion binder. Additionally, the silver matrix lies mostly at the surface of the collodion, some being only loosely bound. The varnish then encapsulates and consequently completes the optical coupling of the silver grains within a 1.5 refractive index medium. Thus, the overcoat and collodion fuse around the silver particles in such a manner that no discrete boundary may be said to exist between them. The degree to which this occurs may well be affected by such factors as the varnish solvent system and the collodion process chemistry. Nevertheless, any attempts to remove a tintype varnish entirely would almost certainly cause the removal of some silver grains.

Whether tintypes employing bleached lac varnishes are more prone to iron corrosion cannot be concluded with certainty. This question might well be explored further in future research. One final remark concerns the cleaning of tintypes. In agreement with the discussion presented earlier on bleached lac manufacture, the saponification of natural resins, and shellac especially, is very easily accomplished with alkali reagents. This suggests that cleaning tintypes using an alkali reagent (e.g., a "mild soap solution"⁶) risks degradation of the varnish surface by converting some portion of it into a saponified state. Such a saponified coating would be more hygroscopic in nature, a condition that would make the plate more susceptible to deterioration.

ACKNOWLEDGEMENTS:

The author wishes to express his gratitude to Melanie E. Feather, conservation scientist, for expert assistance with SEM and EDS analysis and to Martha Goodway, research metallurgist, for her contribution to the author's understanding of the history and technology of iron manufacture.

NOTES:

1. Archer, F.S., "On the Use of Collodion in Photography", The Chemist, Vol II, 1851.
2. Archer, F.S., The Collodion Process on Glass, printed for the Author, London, 1854.
3. Towler, J., The Silver Sunbeam, Facsimile 1864 Edition, Morgan & Morgan, N.Y., 1969.
4. Anon., "Shellac and its Use in Varnishes", British Journal of Photography, Vol 24, No. 893, pp 279-80, 1877.
5. Estabrooke, E M., The Ferrotypes, and How to Make it, Facsimile 1872 Edition, Morgan & Morgan, 1972.
6. Weinstein, Robert A., Booth, Larry, Collection, Use, and Care of Historical Photographs, pg. 165, American Association of State and Local History, Nashville, Tennessee, 1977.

Abstract:

The quality of enclosure materials is of great importance to photographic collections. Basic physical and chemical requirements for enclosures and containers used for processed photographic materials are outlined in ANSI standard IT9.2-1988, "Processed Films, Plates, and Papers - Filing Enclosures and Containers for Storage." Papers and adhesives for enclosures must pass a general photographic activity test. Because previous methods lacked the sensitivity to distinguish between good and only marginally good materials, a much more sensitive test method has been developed during the past six years. This new test method uses very sensitive colloidal silver in gelatin on a polyester support to detect compounds that are aggressive towards the silver image. In addition, a premium-quality, fiber-based photographic paper is used to detect compounds that stain gelatin. The incubation conditions have also been changed in the new test to provide better information in a shorter incubation time. The sensitivity is high enough to allow relative ranking of enclosure quality. The improved photographic activity test has been included in the current ANSI standard.

KEYWORDS

Preservation, enclosure testing, photographic activity test

IMPROVEMENTS TO THE PHOTOGRAPHIC ACTIVITY TEST IN ANSI IT9.2

Douglas W. Nishimura
Image Permanence Institute
RIT City Center
50 West Main Street
Rochester, NY 14614-1274
U.S.A.

Introduction

Processed photographic materials in archival collections require a high degree of individual packaging to protect them. For this purpose a wide variety of paper and plastic materials are commercially available. However, it is essential that these enclosures must not themselves cause harm to the photographic image.

In 1978, the American National Standards Institute (ANSI) published a standard on enclosures for photographic materials setting specifications for the raw materials, design, and nomenclature of enclosures. This standard also specified that all enclosures must pass a general test for chemical interactions known as the Photographic Activity Test (PAT). This test method involved placing the processed photographic material of interest in contact with the enclosure to be evaluated for 30 days at 50°C, 86% RH. Laboratory filter paper, incubated at the same time, served as a control. Passing the test required that changes in the photographic media produced by contact with the enclosure material not exceed changes produced by contact with the control.

The incorporation of the PAT into the ANSI Standard on filing enclosures was a significant step forward, but by 1983, it was recognized that this common-sense test method had many shortcomings.

Deficiencies of the Original Test Method

The main deficiency of the original test method lay in the way it was developed. The test was calibrated using only very bad materials as sources of contamination. As a result, the test did reasonably well in screening out the worst enclosures, but did not accurately discriminate between marginal and very good materials.

At the request of the ANSI committee, the Image Permanence Institute developed a more sensitive PAT which was published in a revised ANSI standard (IT9.2) in 1988. The test method is currently being considered by the International Standards Organization. This paper provides the background data for the improved test.

Detector Selection

There is great variability in the response of different photographic materials to contaminants. Clearly, if the PAT is to have optimum meaning as a standard test, a standardized and sensitive detector is required. Initial work concentrated on finding such a detector.

Harmful interactions with black-and-white photographic images are of two basic kinds: reactions with the silver image to cause fading and other forms of image degradation, and staining of the non-image areas (primarily a reaction with gelatin). Since the reactions which cause image fading and Dmin staining are very different, it was concluded that two detectors would be needed.

(a) Fade Detector

For accurate detection of potential image degradation, the most important attribute of a detector is the micro-structure of its silver image. Those silver materials which show the greatest change in response to the incubation conditions are likely to be the best detectors of image attack. Table I presents the blue filter density changes when samples of processed photographic materials were incubated for 30 days at 50°C, 86% RH. Except for the Agfa colloidal silver coating (which had a starting density of about 1.70), all changes were from an initial density of 1.00.

The colloidal Carey Lea silver coatings on polyester base produced the largest density differences when incubated in contact with known harmful materials and filter paper control. Coatings of this type were described in 1972 by Edith Weyde of Agfa-Gevaert (1) for use as an indicator of oxidizing atmospheres. Coatings

TABLE I

Density of Processed Photographic Materials
after 30 days at 50°C and 86% RH

Detector	Blue Density Change
Conventional Films and Papers	
Kodak 4168 Direct Dupe Film®	0.13
Kodak Polyprint RC Paper®	0.03
Kodak Versalite HCF Film®	0.00
Kodak Azo Paper®	-0.01
Kodak Elite Paper®	-0.01
Kodak AHU 1460 Microfilm®	-0.01
Kodak T-MAT G X-ray Film®	-0.01
Kodak Line Film 2555®	-0.02
Colloidal Silver Materials	
Kodak POP* w/ Heavy Gold Toning	-0.08
Albumen Paper Gold Toned	-0.14
Kodak POP w/ Med Gold Toning	-0.26
Kodak POP w/ Light Gold Toning	-0.40
Agfa Colloidal Silver on Polyester Base	-0.64

* Studio Proof® printing out paper

Table II

Effect of Incubation Conditions on PAT for "bad" Enclosure
Blue Density Change from Filter Paper

Temp	RH	Colloidal Silver Fade Detector			Printing-out Paper Stain Detector		
		15 Day	30 Day	60 Day	15 Day	30 Day	60 Day
50	75	0.04	0.06	-0.01	0.01	0.01	0.03
50	86	0.07	0.11	0.13	0.02	0.02	0.02
50	95	-0.07	0.03	0.11	0.01	0.04	0.05
60	75	0.05	-0.02	-0.03	0.03	0.04	0.06
60	86	0.07	0.22	0.32	0.03	0.04	0.06
60	95	0.02	0.33	0.32	0.05	0.05	0.08
70	75	-0.06	-0.11	-0.19	0.03	0.05	0.08
70	86	0.24	0.20	0.11	0.07	0.09	0.10
70	95	-0.05	0.29	0.10	0.05	0.04	0.06

similar to these were also used by Mary Kay Porter to evaluate adhesives and papers (2). In addition to density changes, the Carey Lea coatings also became mottled in the presence of reactive substances. This localized fading and color change proved to be another useful indicator of harmful enclosures. Consequently Carey Lea silver was chosen as the image fading detector.

(b) Stain Detector

Early experiments showed a significant yellow stain in the Dmin patch of printing-out paper (POP) when incubated with some enclosure materials. This suggested using this material as a stain detector by measuring the increase in blue density. This staining was not necessarily accompanied by image fading in the high density patch, indicating the different nature of the two chemical reactions. Subsequently a premium grade fiber-base photographic print material was used. The essential features are a relatively thick baryta layer and thick emulsion layer. The paper was prepared for use by fixing and thorough washing (without exposure or development), so that it contains no silver and very little residual hypo.

Optimum Incubation Conditions

Since there is a limited amount of silver in the fade detector, the incubation conditions alone, must not produce a sufficiently large density loss that the sensitivity of the detector to poor enclosures is compromised. Therefore it was important to determine the sensitivity of the colloidal silver fade detector to the variables of time, temperature and relative humidity. Both the colloidal silver detector and a lightly gold toned POP stain detector were incubated in contact with an envelope known to have caused severe mirroring and fading under practical conditions. The blue density difference (Table II) between the "bad" enclosure and the control is considered a good measure of the enclosure effect since inherent changes in the detectors are removed.

A positive number indicates that the "bad" envelope faded or stained the sample more than the filter paper. The incubation condition of 15 days at 70°C, 86% RH gave the greatest visual and density differences between the control and the "bad" envelope in the shortest time period.

An analysis of variance (Table III and IV) indicated that temperature had the largest effect followed by RH and time.

Table III

Analysis of Variance for Effects of Time, Temperature, and
Humidity on Fade Detectors in Contact With "bad" Envelope

Source	Sum of Squares	Degrees of Freedom	Mean Square	Variance Ratio	Significance Level
T(emp)	70879.6	2	35439.8	291.1	3.4×10^{-8}
H(umidity)	22919.5	2	11459.8	94.1	0.000003
D(ays)	22054.3	2	11027.2	90.6	0.000003
T X H	2687.6	4	671.9	5.5	0.031174
T X D	3821.5	4	955.4	7.9	0.012991
H X D	310.6	4	77.6	0.6	0.553317
T X H X D	973.9	8	121.7		
Total	123647.0	26			

Table IV

Analysis of Variance for Effects of Time, Temperature, and Humidity on Stain Detectors in Contact With "bad" Envelope

Source	Sum of Squares	Degrees of Freedom	Mean Square	Variance Ratio	Significance Level
T(emp)	14587.0	2	7293.5	269.8	4.6×10^{-8}
H(umidity)	10575.6	2	5287.8	195.6	1.6×10^{-7}
D(ays)	4941.0	2	2470.5	91.4	0.000003
T X H	613.0	4	153.3	5.7	0.029296
T X D	387.0	4	96.8	3.6	0.077597
H X D	469.7	4	117.4	4.3	0.052835
T X H X D	216.3	8	27.0		
Total	31789.6	26			

A second experiment was carried out at the 70°C, 86% RH condition to determine if the 15 day period could be shortened. Four enclosure materials were incubated against both detectors for one, three, seven and fifteen days. Changes in blue density were measured and visual observations for mottling were made. As shown in Table V, broad differentiation between good and bad materials was not achieved until fifteen days of incubation.

Development of Colloidal Silver

Fading of the colloidal silver fade detector as a result of incubation with poor enclosure materials is presumably caused by oxidation of the metallic silver to the ionic form.

To test this hypothesis, thirty enclosure materials were incubated with the colloidal silver detectors for 15 days at 70°C 86% RH. Blue density measurements were made before incubation, after incubation and after development of the detectors in Technidol® for 10 minutes at 63°F. Development of the samples reduces ionic silver to more stable metallic silver, but would not reproduce the original colloidal silver morphology. Therefore it was expected that the faded samples would recover some, but not all of their original blue density after development. This was experimentally verified in Figure 1. In general, the density regained by development is proportional to the loss due to incubation. It is concluded that the fading effect was mainly due to oxidation of the silver and not to morphological changes since the latter would show very little density change after development. However, the spread of data between the thirty enclosure materials decreased after development as shown in the histograms (Figure 2). It was therefore decided that the loss in distinction between materials outweighed the stabilization of the detectors. Consequently development of the fade detectors was not done in subsequent experiments.

Table V

Effect of Incubation Time on PAT
Blue Density Change from Filter Paper

Material	Time	Fade	Stain	Mottling
"Poor" Envelope Paper	1 day	-0.06	0.02	NO
Mat Board #1	1 day	0.02	0.00	NO
Mat Board #2	1 day	0.02	0.00	NO
"Poor" Quality Black Paper Album Page	1 day	0.07	0.02	NO
"Poor" Envelope Paper	3 days	-0.08	0.02	NO
Mat Board #1	3 days	-0.02	0.00	NO
Mat Board #2	3 days	0.04	0.00	NO
"Poor" Quality Black Paper Album Page	3 days	0.08	0.05	YES
"Poor" Envelope Paper	7 days	-0.07	0.03	NO
Mat Board #1	7 days	-0.05	0.01	NO
Mat Board #2	7 days	-0.00	0.02	NO
"Poor" Quality Black Paper Album Page	7 days	0.03	0.08	NO
"Poor" Envelope Paper	15 days	-0.18	0.05	YES
Mat Board #1	15 days	-0.06	0.03	NO
Mat Board #2	15 days	0.17	0.03	YES
"Poor" Quality Black Paper Album Page	15 days	0.07	0.19	YES

Figure 1
Density Loss from Incubation Versus
Density Gain from Development

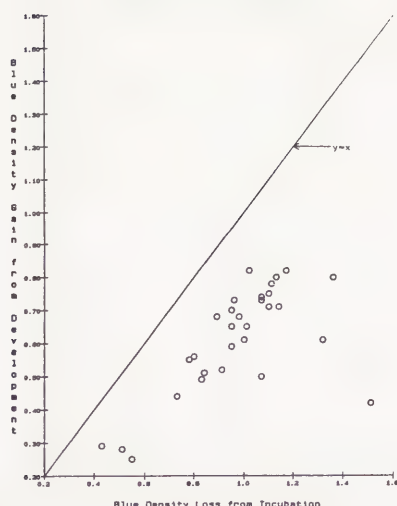


Figure 2
Effect of Developing the Fade Detector After Incubation
N = 30 enclosure materials

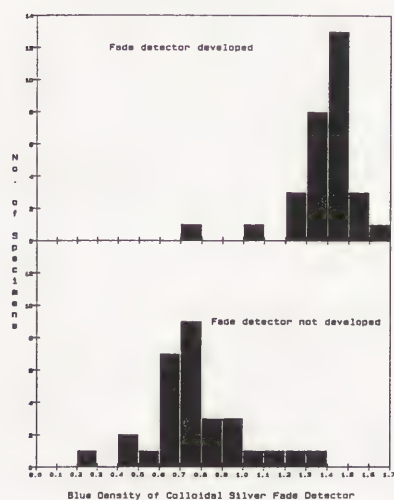


Table VI

Effect of Conditioning Enclosure Materials in PAT
Density Change from Filter Paper

Enclosure	Fade Detector		Stain Detector	
	Unconditioned	Conditioned	Unconditioned	Conditioned
1	0.00	-0.01	0.00	-0.01
2	0.03	0.04	0.00	0.00
3	0.01	0.07	0.01	0.00
4	0.08	0.12	0.00	0.01
5	-0.07	-0.02	0.02	0.02
6	-0.04	-0.02	0.03	0.03
7	-0.08	0.01	0.06	0.03
8	-0.11	-0.07	0.04	0.03
9	-0.09	-0.06	0.04	0.02
10	-0.14	-0.11	0.03	0.02

Pass/Fail Limits

The usefulness of the PAT is its ability to determine if an enclosure is acceptable for photographic materials. Even good materials are not expected to perform as well as filter paper and therefore, pass/fail limits have to allow changes greater than that observed with filter paper. There are three criteria for passing the test, (1) stain, (2) fade and (3) the absence of mottling.

(1) The stain detector consistently had very even changes across the whole strip. The pass/fail criteria for stain was set at the mean stain caused by the control plus 0.05 density units. (2) The fade detector had a slight variability in silver density over its total area which caused small variations in the amount of density lost during incubation. The pass/fail criteria was therefore set at the fade caused by the control plus two standard deviations of this control. (3) The absence of mottling was made another criteria of this test.

Specimen Conditioning

Good scientific method suggests that both the test samples and detectors should be conditioned to the incubation humidity before the test is started. In theory, if harmful materials in the enclosures are carried by moisture, then pre-conditioning of samples would make the test more sensitive. However, an enclosure - detector sandwich will obtain complete conditioning within a fraction of the 15 day incubation time. Nevertheless, a conditioning experiment was done in which ten different enclosures and detectors were conditioned to 86% RH before assembly into sandwiches. Surprisingly, experiments showed that conditioning made the test less sensitive (Table VI). Possibly deleterious materials escaped during the conditioning period. Since conditioning the materials prior to sandwich assembly is difficult and decreases the sensitivity of the test, this procedure is not followed.

Specimen Thickness

Another question was whether the enclosure thickness would affect the test result. If a thick material provides any barrier to moisture penetration, then thick mat boards would be expected to perform better than thin boards. However, if moisture penetrates any thickness sufficiently in fifteen days, then thick boards (containing more harmful material) would perform worse than thin boards. Results showed that thicker boards tended to perform

Table VII

Density Change from Filter Paper Laminated
with Various Adhesives

Plies	Adhesive	Fade Detector	Stain Detector
2	Polyvinyl Acetate	-0.97	0.08
4	Polyvinyl Acetate	-0.94	0.09
8	Polyvinyl Acetate	-0.96	0.08
2	wheat starch	-0.96	0.08
4	wheat starch	-0.93	0.10
8	wheat starch	-0.88	0.09
2	Methyl Cellulose	-0.96	0.10
4	Methyl Cellulose	-0.93	0.08
8	Methyl Cellulose	-0.89	0.08
2	No Adhesive	-0.95	0.08
4	No Adhesive	-0.93	0.09
8	No Adhesive	-0.89	0.09

Table VIII

Density Change of Conditioned and Unconditioned
Mat Boards (Without Adhesive) in PAT

Material	Plies	Conditioned		Unconditioned	
		Fade Det.	Stain Det.	Fade Det.	Stain Det.
Filter Paper	1	-1.01	0.08	-1.00	0.09
	2	-0.96	0.09	-0.97	0.09
	4	-0.93	0.09	-0.99	0.10
	8	-0.88	0.11	-0.92	0.09
Mat Board #1	1	-1.02	0.11	-1.07	0.11
	2	-1.02	0.12	-1.04	0.12
	4	-0.99	0.12	-1.08	0.15
Mat Board #2	1	-1.07	0.12	-1.11	0.13
	2	-1.06	0.11	-1.09	0.13
	4	-1.11	0.11	-1.14	0.12

Table IX

Effect of Pressure on Photographic Activity Test

Material	Pressure	Fade Detector Blue Density	Fade vs Filter Paper	Stain Detector Blue Density	Stain vs Filter Paper	Mot- tling	Pass/ Fail PAT
Filter	0.66 g/cm ²	-1.01		0.10		NO	-
Paper	5.42 g/cm ²	-1.00		0.09		NO	-
	50.00 g/cm ²	-1.04		0.09		NO	-
"Bad"	0.66 g/cm ²	-0.99	-0.02	0.14	0.04	YES	FAIL
Envelope	5.42 g/cm ²	-1.14	0.14	0.14	0.05	YES	FAIL
Paper	50.00 g/cm ²	-1.29	0.25	0.19	0.10	YES	FAIL
Mat	0.66 g/cm ²	-1.03	0.02	0.13	0.03	NO	PASS
Board	5.42 g/cm ²	-1.03	0.03	0.13	0.04	YES	FAIL
#1	50.00 g/cm ²	-1.18	0.14	0.13	0.04	YES	FAIL
Mat	0.66 g/cm ²	-0.94	-0.07	0.13	0.03	NO	PASS
Board	5.42 g/cm ²	-0.91	-0.09	0.13	0.04	NO	PASS
#2	50.00 g/cm ²	-0.90	-0.14	0.13	0.04	NO	PASS

slightly better than thinner boards (Table VII) but the differences were very small. However these small differences can not be attributed to lack of moisture conditioning since conditioning did not make thick and thin boards perform more evenly (Table VIII).

Sandwich Pressure

Pressure in the enclosure-detector sandwich was the final variable that was studied. High pressure made more materials fail due to mottling and fading, but also caused a greater problem with fibers sticking to the colloidal silver detector (Table IX). Low pressure allowed even very poor materials to pass the fading and mottling criteria. Based on the experimental results, a pressure of 5 g/cm² was selected for the test method.

Test Procedure

The standardized test method involves incubating two strips of each detector in contact with the enclosure specimen in a sandwich for 15 days at 70°C, 86% RH. Status A blue diffuse density measurements are made at four locations on each detector: transmission on the fade detectors and reflection on the stain detectors. In addition to the detectors and specimens, uncoated polyester, glass and stainless steel weights are required. The detectors, specimens and polyester are all cut to 2 X 12 cm strips. Each detector is put face to face with an enclosure sample and each pair is isolated with polyester. Note that the fade detector-enclosure pair only needs one piece of polyester, since the fade detector is already on a polyester base. Similar stacks are made using Whatman #1® filter paper instead of the enclosure material. Glass strips are used at the top and bottom of each sandwich. Finally, stainless steel weights supplying a pressure of 5 g/cm² are added at the very top of each sandwich.

Practical Application of the New Photographic Activity Test

To illustrate the use of the P.A.T. in the selection of enclosures, an experiment was performed in which 90 different enclosures were evaluated. This included 66 commercially available materials which could be considered "archival," not by any strict definition, but because they were sold by suppliers specializing in this line of products. The archival materials included 36 rag boards, 9 non-rag boards, and 21 papers. These materials were obtained from a number of manufacturers and distributors and are representative of the kinds of products that might be used in archival collections. Also included were a number of known good and bad materials.

The outcome of the test for the 66 archival products is given in Table X. Overall, 29 (44%) of the archival products passed the P.A.T. The most common cause of products failing the P.A.T. was mottling. In all, 25 products (38%) failed the mottling criterion. Mottling represents the presence of local "hot spots" of fading and generally indicates inhomogeneity in an enclosure product.

Figure 3 is a frequency histogram of the performance of the 66 archival products in the fading criterion. The horizontal axis values are the mean fading of the products relative to the control. The positive values on the horizontal axis indicate less fading than the control. Note that the distribution of fade data is approximately normal. Overall, 16 (24%) of the archival products failed the fading criterion.

Table X

Summary of PAT Results
on 66 Archival Products

FADE	STAIN	MOTTLE	NO.	%
FAIL	FAIL	FAIL	1	2
PASS	FAIL	FAIL	4	6
FAIL	PASS	FAIL	8	12
FAIL	FAIL	PASS	0	0
PASS	PASS	FAIL	12	18
FAIL	PASS	PASS	7	11
PASS	FAIL	PASS	5	8
PASS	PASS	PASS	29	44

Figure 3

Distribution of Fade Data
for 66 Archival Products

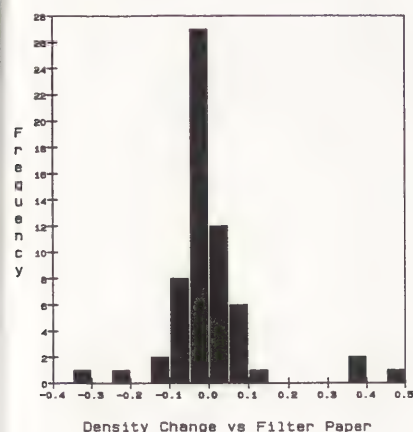


Figure 4

Distribution of Stain Data
for 66 Archival Products

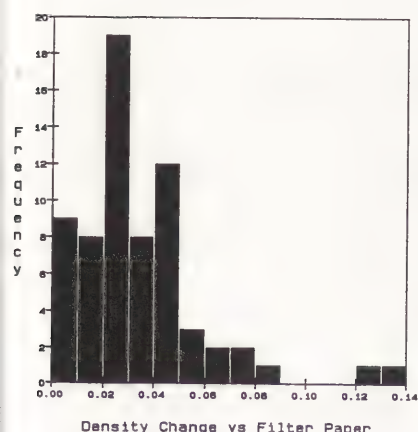


Figure 4 is a frequency histogram of stain data for the 66 archival products. The horizontal axis values are the measures of stain relative to the filter paper control. None of the products stained less than the control, but most were less than the 0.05 limit for passage of the test. Overall, 10 (15%) of the archival products failed the staining criterion.

This evaluation of archival products give an important lesson for archive managers: Not all enclosures offered in the marketplace are safe to use with photographs. Vague descriptors such as "acid free" do not guarantee inertness toward photographs. By insisting that enclosure manufacturers demonstrate compliance with ANSI IT9.2-1988, consumers can provide themselves with reasonable assurance of satisfactory performance.

Performance of Archival Products in Perspective

The performance of the 66 archival products can be put into perspective by comparing them with the behavior of some of the 24 known good and bad materials included in this test. This data illustrates that generally, photographic materials have come a long way from the dreadful materials that were so common in the past. But it is also important to note that the fourth worst fading performance of all 90 materials was given by an "archival" 2-ply white rag board. Two out of the three Japanese tissues tested failed the fading criterion. There appeared to be no difference in performance related to the presence or absence of carbonate buffering. Although the PAT is a demanding and rigorous test method, there are numerous products on the market which meet its requirements and are demonstrably safe to use in archives.

Conclusions

An improved Photographic Activity Test was developed based on the use of both colloidal silver on polyester film base and fixed-out fiber-base prints as detectors of fade and stain respectively. The incubation conditions are 15 days at 70°C, 86% RH with a sandwich pressure between enclosure materials and detectors of 5 g/cm². The blue filter density change was measured in both the colloidal silver and the fiber-base print paper. In addition to fade and stain limits, the enclosure shall not cause any mottling in the colloidal silver. The details of this new Photographic Activity Test are now standardized in ANSI Standard IT9.2-1988.

References

- 1) Weyde, Edith, "A Simple Test to Identify Gases Which Harm Silver Images," Photographic Science and Engineering 16, no. 4 (1972): 283-286.
- 2) Mary Kay Porter, Private Communication, 1983.

Acknowledgments

The authors would like to thank the National Endowment for the Humanities, the National Historical Publications and Records Commission, and the National Museum Act for funding this research. Also we are grateful to Agfa-Gevaert and to the Conservation Branch, National Archives and Records Administration, for help with the project.

Materials

Kodak 4168 Direct Duplicating Film®
 Kodak Polyprint RC Paper®
 Kodak Versalite HCF Film®
 Kodak Azo Paper®
 Kodak Elite Paper®
 Kodak AHU 1460 Imagecapture Microfilm®
 Kodak T-MAT G X-ray Film®
 Kodak Line Film 2555®
 Kodak Studio Proof Paper®
 Kodak Technidol Developer®

Eastman Kodak
 Rochester, NY 14603
 (716)-724-4000

Whatman #1 Filter Paper®

Whatman Inc.
 9 Bridewell Place
 Clifton, NJ 07014
 (201)-773-5800 Telex 133426

Working Group 9

Textiles

Textiles



Abstract

A review is presented of the work done by characterizing some degraded historic silk flags from the National Museum of American History, Smithsonian Institution, Washington, D.C. (14 samples) and from the Capitol Preservation Committee, Harrisburg, Pennsylvania (34 samples). Data reviewed are elemental analyses obtained by energy dispersive x-ray spectrometry (EDS), percent ash percent sulfur, pH by modified cold extraction, and dye analyses. Only one sample proved to be weighted with inorganic matter. Possible sources of degradation are discussed and suggestions are made for further study.

Keywords: silk, EDS, degradation, dyes

RECENT RESULTS CONCERNING THE DEGRADATION OF HISTORIC SILK FLAGS

Mary W. Ballard, Smithsonian Institution, Washington, D.C.

Robert J. Koestler, Metropolitan Museum of Art, New York, N.Y.

Norman Indictor, Brooklyn College and Graduate Center, CUNY, Brooklyn, N.Y.

Introduction

The degradation of nineteenth century silks is a special problem for textile historians, curators, and especially conservators. At both the Smithsonian Institution and the National Archives, Washington, D.C. are records of examination as early as 1880, in which silk flags are listed in "poor condition." These flags, dating from the American Civil War, 1861-1865, were assumed to have been made from weighted silks, that is, from silks which were permitted to absorb substances (usually inorganic salts) in their manufacture for the purpose of increasing the weight and body of the material as well as to render the silk more easily susceptible to dyeing or painting. The presence of weighted silks as a common constituent of flags was generally not demonstrated as curators and conservators were reluctant to sacrifice the required sample (ca. 2-3 grams; ca 600-700 cm²)^{1,2,3}.

Recently procedures have been described from our laboratories which permit analyses on semi-micro and micro samples (ca. 1-2 mm²) for the estimation of inorganic silk weighting. Standard samples were prepared based on nineteenth and twentieth century silk technology texts. The analytical procedures involved use of energy dispersive x-ray spectrometry (EDS), or, more generally, any microprobe technique, and determination of ash content (ca. 0.1-0.2 g). Correlation between the recipes (various levels of iron, tin, and other inorganic substances) and the analyses were unerring.⁴

National Museum of American History Samples

Results from fourteen historic flag samples dating from 1863 to about 1920 obtained from the National Museum of American History, Smithsonian Institution indicated that only one sample (W10, Tables 1 and 2) was tin weighted. All the samples had high sulfur content. There was no clear-cut relationship between the colors of the samples and the inorganic elements present suggesting that no standard process was used in coloring the flags. Dye analyses of a few of these samples indicated C.I. Acid Red 26 and C.I. Acid Red 88 in two of the red samples and C.I. Acid Blue 93 for one of the blue samples. These synthetic dyes have sulfonic acid groups, but probably not enough to account for the high sulfur content. Even undyed (cream) samples contained high levels of sulfur.⁵

Possible explanation for the high sulfur content of these flags are: previous conservation treatments (none documented); air pollution; storage conditions; original silk processing. Silk bleaching in the nineteenth century was, in fact, carried out with "sulphurous acid."⁶

Harrisburg Samples

The Capitol Preservation Committee at Harrisburg, Pennsylvania provided a second sample set for evaluation. The set of Civil War flags (1861-1865) was a more coherent set whose history and manufacture is often documented (Table 3). EDS analyses were obtained for elements present above atomic number 11 (Table 4); dye analyses were performed; and percent sulfur, ash, and pH (Table 5) were also obtained.⁷

Sulfur was again present in all samples. None of the samples was weighted with inorganic material. Sulfur content was about two to nine times the amount found in fibroin⁸ with most samples containing about five times the amount found in new, degummed specimens. Considerable variation was found in elemental composition (EDS, elements of greater than atomic number eleven) and therefore no standard methods for processing the silks was suggested from these results. All the red samples proved to be cochineal (C.I. Natural Red 4) and all the blue samples were Prussian Blue (C.I. Pigment Blue 27).^{9,10} Even though the dye types in this group were consistent, the variety of elements found again suggest non-uniform procedures in the manufacture of the textiles. A possible source of diverse

compositions may be the idiosyncratic use of auxiliaries that have accompanied the dyeing processes and are sometimes clearly indicated in the literature, but more often only alluded to without precise recipe.^{11,12} pH measurements for this group of samples showed a barely discernible (insignificant) color specificity of 4.16 ± 0.3 white; 4.2 ± 0.3 red; and 4.8 ± 0.5 blue. All values were significantly lower by about 2.0 pH units than those obtained for modern silk. Anecdotal evidence attributable to American textile conservators indicates that white silk is usually more shredded than red, and red is more shredded than blue. This group also showed a color specificity (significant) to ash content: $1.6 \pm 3\%$ white; $3.2 \pm 1.0\%$ red; and $4.9 \pm 0.4\%$ blue.

Advancing Technology's Effects on Nineteenth Century Silks

In addition to such practices as bleaching⁶ and the imaginative use of auxiliaries^{11,12} in order to exhaust dye baths during the nineteenth century, another practice, "brightening" (*Fr. avivage*), was a way of enhancing luster and the "hand" of the material. In a final rinse, tartaric acid (the most expensive), acetic acid (the most fugitive), or sulfuric acid (the most common) was used in the wash waters.^{13,14} In fact, sulfuric acid became a common chemical, cheap, omnipresent, and readily available to the textile industry during the nineteenth century. It was widely used for all aspects of textile processing--bleaching, mordanting, dyeing, brightening--as well as in the actual manufacture of dyes and dye intermediates.¹⁵ By the end of the nineteenth century forty of the sixty most important early synthetic dyes in western Europe were fixed to the fiber (silk or wool) in the presence of sulfuric acid.¹⁰ The use of sulfuric acid as an important chemical in the production of dyes, intermediates, and as an auxiliary in the processing of textiles continues today.¹⁶⁻¹⁸

In traditional dyeing the conditions that require acidic conditions in the dye pot were achieved through the natural low pH of the waters employed, from the accompanying acidity of the natural product from which the dye was derived, or from a naturally acid auxiliary (e.g. tannins, fruit skins). The use of mineral acids as auxiliaries to dyeing was not prevalent until the nineteenth century.¹⁹ Sulfuric acid production in large quantities with easy distribution is, in fact, a leading product of the Industrial Revolution and accompanies the growth and development of dye and textile technologies throughout Europe.^{20,21}

Another possibility of accounting for the unusually degraded condition of nineteenth century silks may be more efficient or more thorough "degumming" of the silk,²² the wash which comes early in the processing of silk fiber to remove much of the waxy sericin for the sake of enhancing the dyeability of the silk fibers. Although a vigorously degummed product may have many manufacturing advantages, the longevity of the product may suffer since the sericin probably provides some long-term flexibility for the fibers and may even play some part in inhibiting autoxidation or solvolytic degradation. The degraded condition of the American nineteenth/twentieth century flags may be at least in part attributable to Industrial Revolution technologies.

Other possibilities which suggest sources of degradation are the continued presence of gunpowder²³ and dirt residues connected to the historic contexts of the objects. Salt (NaCl) deliquescence of nineteenth century silk objects framed under glass has been observed for a number of examples²⁴ suggesting a processing of silk which would have incorporated salt at some time in its manufacture. The exact reasons for this, its frequency, and implications for degradation and conservation treatment require further investigation.

Future Study

Although reports suggests that delicate aqueous treatment may have a strengthening effect on shattered silk, enabling the handling of otherwise too friable fibers,²⁵ the possibilities of loss of information and subsequent degradation must be taken into account. Problems of storage conditions and exhibition become important as these materials become objects of public and scholarly attention. Flags in general are objects of clearcut iconographic and historic significance and are often attended by documentation far beyond what is available for most museum textiles. However, the size and condition of most nineteenth and twentieth century examples make prolonged or extensive display nearly impossible. Protocols for display and storage, access and study, are being addressed for both the Harrisburg collection and the National Museum collection.²⁶

Directions for future research on historic flags have been suggested at a recent conference held at the Conservation Analytical Laboratory, Smithsonian Institution, Washington, D.C. in November 1989.²⁷

1. Examination of additional groups of historic American Flags in order to characterize the degradation and to note aspects of manufacture of such objects. The silk of seventeenth and eighteenth century flags (and other silks) is reputed to be in better condition than nineteenth/twentieth century flags. Objective observations of relative deterioration: red vs. white vs. blue may help in the understanding of silk deterioration. It is clear that the general phenomenon of shattered silk is not just a flag problem; the information obtained for flags would be useful for other silk problems.

2. Examination of additional groups of historic flags from Europe, Asia, and western hemisphere countries outside the United States in order to describe geographic features of manufacture and degradation. Some European material has been reputed to be weighted silk. Historic and geographic parameters for silk manufacturing processes may be revealed during the course of such a study.

3. Examination of non-textile materials associated with the flags: fringes, metallic paint, wooden poles, adornments, etc. These materials are all part of the artifact and their interaction with the textiles is important to monitor. Their degraded condition must be addressed as part of the conservation problem.

4. Examination of the components of modern flags and recording of current manufacturing practices in order to anticipate future degradation problems.

5. Forensic examination of selected examples to determine the extent and identity of historic soilings (powder burns and residues) may provide useful information for decisions concerning cleaning and treatment of flags.

6. Determination of the fate of specific functional groups or amino acid moieties of the silk in historic examples may shed light on the mechanism of degradation and suggest possible treatments. The chemical implications of high sulfur content in the shattered silks may provide clues to a more generalized description of silk degradation.

7. Comparison of the amounts of sericin in shattered silks with sericin in silks that seem to be in better condition may suggest causal relationships for the condition of the silks and possible treatments.

8. Monitoring of surface pH and objective color of historic silks may provide clues and warning signals to continuing environmental influences on the degradation of silks. A protocol for obtaining the surface pH (similar to that for the surface pH of paper) appropriate for historic silks would have to be established.

9. Study of the effect of water treatment on shattered silks in light of reports that shattered silks are more easily handled after aqueous treatment.

NOTES

- 1 J. Branegan, "Practical Analysis of Methods for Determination of Artificial Weighting of Tin Weighted Silk," *The Melliand* vol. 1, #5 (1929):735-739.

- 2 H.J. Hoffman, "Qualitative Spot Tests," *Analytical Methods for a Textile Laboratory*, ed. by J.W. Weaver (Research Triangle Park, North Carolina: American Association of Textile Chemists and Colorists, 1984).

- 3 P.A. Koch, *Microscopic and Chemical Testing of Textiles*, transl. C.J. Hooper (New York: Textile Book Service, 1963).

- 4 M. Ballard, R.J. Koestler, and N. Indictor, "Weighted Silks Observed with Scanning Electron Microscopy-Energy Dispersive X-Ray Spectrometry (SEM-EDS)," *Scanning Electron Microscopy* vol. 2 (1986): 499-506.

- 5 M. Ballard, R.J. Koestler, C. Blair, and N. Indictor, "Historic Silk Flags Studied by Scanning Electron Microscope--Energy Dispersive X-Ray Spectrometry (SEM-EDS)," *Archeological Chemistry IV*, ed. R. O. Allen, *Advances in Chemistry Series #220* (Washington, D.C.: American Chemical Society, 1989), pp. 134-142.

- 6 E. Knecht, C. Rawson, and R. Loewenthal, *A Manual of Dyeing*, 2nd edition (London: Charles Griffin and Co., Ltd., 1910) vol. 1, pp. 160-161.

- 7 M. Ballard, R. J. Koestler, C. Blair, C. Santamaria, and N. Indictor, "Historic Silk Flags from Harrisburg," *Historic Textiles and Paper Materials II: Conservation and Characterization*, eds. S.H. Zeronian and H.L. Needles, ACS Symposium Series #410 (Washington, D.C.: American Chemical Society, 1989) pp. 134-142.

- 8 M.S. Otterburn, "The Chemistry and Reactivity of Silk," *Chemistry of Natural Protein Fibers*, ed. R.S. Asquith (New York: Plenum Press, 1977) p.56.

- 9 M. Saltzman, "The Analysis of Dyes in Museum Textiles, or You Can't Tell a Dye by its Color," *Textile Conservation Symposium in Honor of Pat Reeves*, eds.

C.C. McLean and P. Connell (Los Angeles, California: The Conservation Center, Los Angeles County Museum of Art, 1986) pp. 34-35.

10. H. Schweppe, *Practical Information of Early Synthetic Dyes, Practical Hints on Dyeing with Early Synthetic Dyes* (Washington, D.C.: Conservation Analytical Laboratory, Smithsonian Institution, 1987).

11. Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, vol. 1, p. 273.

12. *Ibid.*, vol. 2, p. 696.

13. *Ibid.*, vol. 1, 64.

14. A. Ganswindt, *Dyeing Silk, Mixed Silk Fabrics and Artificial Silks*, transl. C. Salter. (London: Scott, Greenwood and Son, 1921), p.86.

15. Knecht, Rawson, and Loewenthal, *A Manual of Dyeing*, vol. 1, p. 166.

16. J.L. Rush, "Dyeing with Acid Dyes," *Dyeing Primer* (Research Triangle Park: American Association of Textile Chemists and Colorists, 1981), pp. 7-9.

17. C.L. Bird, *The Theory and Practice of Wool Dyeing*, 4th ed. (Bradford, Yorkshire: Society of Dyers and Colourists, 1974).

18. C.H. Giles, *A Laboratory Course in Dyeing*, 3rd ed. (Bradford, Yorkshire: Society of Dyers and Colorists, 1974), pp. 80-82.

19. H. Schweppe, *Practical Hints on Dyeing with Natural Dyes* (Washington, D.C.: Conservation Analytical Laboratory, Smithsonian Institution, 1986).

20. C. Singer, E.J. Holmyard, A.R. Hall, and T.I. Williams, eds., *A History of Technology*, vol. 4, *The Industrial Revolution c. 1750 to c. 1850*, (Oxford: Clarendon Press, 1958), pp. 242-245.

21. *Ibid.*, vol. 5, *The Late Nineteenth Century c. 1850 to c. 1900*, pp. 244-248.

22. N. Indictor and M. Ballard, "The Effects of Aging on Textiles that Contain Metal: Implications for Analyses; Problems Encountered in Conservation," (in press).

23. J. Butler, Explosives Analysis Unit, Federal Bureau of Investigation, Washington, D.C., 1987; C. Tumosa, Conservation Analytical Laboratory, Smithsonian Institution, Washington, D.C. 1989, private communications.

24. T. Padfield and D. Erdhardt, "The Spontaneous Transfer to Glass of an Image of Joan of Arc," in *8th Triennial Meeting ICOM Committee for Conservation Preprints* (Los Angeles, California: The Getty Conservation Institute, 1987), pp. 909-915.

25. E. Keyserlingk, Canadian Conservation Institute, private communication, 1989.

26. D. Kloster, S. Thomassen-Kraus, J. Harris, National Museum of American History, Smithsonian Institution, Washington, D.C.; D. Kessler, R. Sauers, K. Lafaver, Harrisburg Flag Preservation Project, Harrisburg, Pennsylvania, private communications, 1989.

27. Participants in the conference, in addition to the authors, included: Conservation Analytical Laboratory, Smithsonian Institution: N. Tuross (CAL/NIH), M. Becker (CAL/John Hopkins), C. Tumosa, D. Erhardt, A. Bowes, S. Collins; National Museum of American History, Smithsonian Institution: D. Kloster, S. Thomassen-Kraus, K. Harris; Canadian Conservation Institute: E. Keyserlingk; Costume Institute, Metropolitan Museum of Art: C. Paulocik; Harrisburg Flag Preservation Project, Harrisburg, Pennsylvania: D. Kessler, R. Sauers, K. Lafaver; National Centre of Museums, Budapest: A. Timár-Balázsy.

TABLE 1: Natural Museum of American History Flags: Ash Content

Sample	Catalog No.	Inv. No.	Color	Date	%Ash ^a
W1	81711W14	-	Cream	1877-90	0.61
W2	81711W14	-	Cream	1877-90	0.50
W3	Unknown	-	Cream	Unknown	- ^b
W4	81711W10	64127	Red	1863-65	2.79
W5	81711W10	64127	Cream	1863-65	1.13
W6	81745W06	-	Blue	ca. 1884	0.42
W7	81745W07	-	Red	1896-08	1.32
W8	81745W07	-	Cream	1896-08	1.77
W9	81759W59	-	Cream	1863-65	1.81
W10	Unknown	-	Cream	WW1	46.49
W11	RWW81759W52	-	Red	1912-20	4.32
W12	81745W00	69143	Blue	1875-00	0.89
W13	81711W11	-	Blue	1883-88	0.37
W14	Unknown	-	Cream	Unknown	- ^b

^a Samples burned under Oxygen at 900-1000°C, ca. 0.5 hr.

^b No sample taken

TABLE 2: National Museum of American History Flags: EDS Results

<u>Sample</u> <u>No.</u>	<u>Na</u>	<u>Mg</u>	<u>Al</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>Cl</u>	<u>K</u>	<u>Ca</u>	<u>Fe</u>	<u>Sn</u>
W1	-	-	+	+	-	++	-	(+)	+	+	-
W2	-	-	-	+	-	++	-	(+)	(+)	(+)	-
W3	-	-	-	+	-	++	-	-	+	-	-
W4	+	(+)	+	+	-	++	-	(+)	+	(+)	-
W5	+	-	+	+	-	++	(+)	+	+	-	-
W6	-	-	-	+	-	++	+	(+)	+	-	-
W7	-	-	+	+	-	++	-	-	+	-	-
W8	-	-	-	+	-	++	+	+	+	-	-
W9	+	(+)	+	+	(+)	++	(+)	+	+	(+)	-
W10	+	(+)	-	+	+	(+)	-	-	-	-	++
W11	-	(+)	(+)	+	(+)	++	-	-	+	(+)	++
W12	-	-	(+)	+	-	++	(+)	(+)	+	+	-
W13	-	-	+	+	-	++	-	(+)	+	(+)	-
W14	-	-	+	+	-	++	-	(+)	+	+	-

++ Present in significant amounts (> 30% of elements of atomic no. > 11)

+ Present

- Absent (not detected)

(+) Possible present (ca. 5% of elements of atomic no. > 11)

TABLE 3: Description of Harrisburg Flags Samples

<u>No.</u>	<u>Registra- tion No.</u>	<u>Regiment</u>	<u>Historical Name</u>	<u>Manufacturer</u>
012	1985.012	23rd PA	State Color	Evans & Hassall
019	1985.019	28th PA	State Color	Evans & Hassall?
022	1985.022	29th PA	State Color	Horstmann Bros. & Co.
026	1985.026	31st PA (2nd res)	State Color	Horstmann Bros. & Co.
096	1985.096	63rd PA	State Color?	Evans & Hassall?
137	1985.137	82nd PA	State Color	Unknown
175	1985.175	Unknown	State Color	Evans & Hassall?
066	1985.066	51st PA	State Color	Horstmann Bros. & Co.
167	1985.167	51st PA	Guidon, National	Unknown
168	1985.168	51st PA	Guidon, National	Unknown
005	1985.005	59th PA (2nd Cav)	State Standard	Horstmann Bros. & Co.
050	1985.050	44th PA (1st Cav)	State Standard	Unknown
002	1985.002	78th PA	National Regimental	Unknown
103	1985.103	67th PA	National Regimental	Unknown

TABLE 4: Qualitative EDS Results on Harrisburg Flags

<u>Sample</u> <u>No.*</u>	<u>Na</u>	<u>Mg</u>	<u>Al</u>	<u>Si</u>	<u>S</u>	<u>Cl</u>	<u>K</u>	<u>Ca</u>	<u>Fe</u>	<u>Sn</u>
012R	+	-	(+)	+	+	(+)	+	+	+	-
W	(+)	-	(+)	+	+	(+)	+	+	(+)	-
B	(+)	(+)	(+)	(+)	+	(+)	-	+	++	++
019R	(+)	(+)	(+)	+	+	-	(+)	+	+	+
W	(+)	-	(+)	+	++	(+)	(+)	+	(+)	+
B	(+)	(+)	(+)	+	+	-	-	+	++	++
022R	(+)	-	(+)	+	+	-	(+)	+	+	+
W	(+)	-	(+)	+	+	(+)	+	+	+	-
B	(+)	-	(+)	(+)	+	(+)	-	+	++	++
026R	(+)	-	+	+	+	-	+	+	+	(+)
W	-	-	+	+	+	(+)	+	+	+	-
B	(+)	-	(+)	+	+	-	+	+	++	+
096R	(+)	-	+	+	+	+	+	+	+	(+)
W	(+)	-	+	+	+	+	+	+	+	-
B	(+)	-	(+)	+	+	(+)	+	+	++	++
137 R	(+)	-	+	+	+	(+)	+	+	+	-
W	(+)	-	(+)	+	+	(+)	+	+	+	-
B	-	-	(+)	+	+	(+)	-	+	++	++
175R	+	-	+	++	+	+	+	+	+	(+)
W	-	-	+	+	++	(+)	+	+	+	-

Table 4 Continued

B	(+)	-	(+)	+	+	(+)	-	(+)	++	++
066R	(+)	-	+	+	+	(+)	-	+	+	++
W	(+)	-	+	+	+	(+)	+	+	+	-
B	(+)	(+)	(+)	(+)	+	(+)	-	(+)	++	++
167R	(+)	-	(+)	+	+	-	-	+	(+)	++
W	-	-	(+)	+	++	(+)	-	+	+	+
B	-	-	(+)	++	++	(+)	(+)	+	+	-
168R	(+)	-	(+)	+	+	(+)	+	+	+	+
W	-	(+)	(+)	+	++	-	+	+	+	-
B	-	(+)	(+)	+	++	(+)	(+)	++	(+)	-
005B	(+)	(+)	(+)	+	+	-	(+)	(+)	++	+
050B	-	-	+	+	+	-	-	+	+	+
002B	+	-	(+)	+	+	+	(+)	+	+	+
103B	+	-	+	+	+	(+)	(+)	+	+	+

*RWB refers to color of samples

++ Present in significant amounts (>30% of elements of atomic no. >11)

+ Present (ca. 5-30% of elements of atomic no. >11)

- Absent (not detected)

(+) Possibly present (ca. 5% or less of elements of atomic no. >11)

TABLE 5: pH, Sulfur, Ash of Harrisburg Flags

<u>Sample No.</u>	<u>pH^a</u>	<u>Sulfur^b %</u>	<u>Ash^c %</u>
Blue Samples			
012	4.61	0.071	5.95
019	4.97	0.27	6.49
022	5.18	0.19	7.52
026	4.60	0.36	4.75
096	4.86	0.30	5.62
137	4.64	0.33	<0.1*
175	4.17	0.32	5.49
066	5.30	0.15	5.44
167	4.15	0.30	<0.3*
168	4.08	0.34	<0.6*
005	4.81	0.28	5.15
050	5.28	0.18	7.72
002	4.85	0.35	5.11
103	5.35	0.38	7.21
Red Samples			
012	4.08	0.15	3.62
019	3.87	0.37	<2.8*
022	4.28	0.16	1.76
026	3.88	0.33	2.75
096	4.25	0.24	4.30
137	4.19	0.17	2.73
175	4.31	0.47	4.79
066	4.77	0.31	n.d.
167	3.86	0.30	2.28
168	4.29	0.23	<2.9*
White Samples			
012	n.d.	0.46	1.84
019	n.d.	0.28	0.83
022	n.d.	0.23	1.03
026	n.d.	0.42	1.66
096	4.41	0.39	3.65
137	n.d.	0.31	1.75
175	3.79	0.42	1.26
066	n.d.	0.15	1.33
167	3.97	0.31	1.25
168	n.d.	0.66	1.94

^a Modified cold extraction^b Total sulfur: S converted to methylene blue, determined spectrophotometrically^c Samples burned under oxygen at 900-1000° C, ca. 0.5 hr.

* Sample <0.2 mg

n.d. no data

ABSTRACT

The conservation/restoration of an historical Prussian double-leaf standard of 1798 made great demands on practical skill and theoretical knowledge. In the first place there was the restoration of the silk ground of the relief embroidery, preserved only in fragments. The expansive missing parts were filled in and covered up in addition with reinforced silk crêpe around the relief embroidery. Further problems arose in removal with the reinforcement of old restorations of the years 1813 and 1900. Thanks to this work the original character of the standard could be restored to a large extent. The analyses constituted a major problem in the treatment of the standard. This revealed the significance of the consideration of the historical background in regard to a successful conservation/restoration.

KEYWORDS

Textile restoration, double leaf standard, relief embroidery/silk ground, Liberation Wars 1813/15, removal of old restorations, material technological analyses.

CONSERVATION AND RESTORATION OF A DOUBLE-LEAF STANDARD - SILK GROUND WITH RELIEF EMBROIDERY -

Eva Fischer, Brigitte Krüger
Museum of German History
Unter den Linden 2
Berlin
1086
GDR

Art Historical and Analytical Description

The stocks of the Museum of German History in Berlin include a Prussian standard dating from the year 1798 (1). This was the regimental standard of the royal cuirassiers; it was owned by the "Garde du Corps" regiment, an important witness of Prussian-German military history. The cuirassier regiment "Garde du Corps" (1740 - 1918), an élite troop of Prussia, carried the standard, awarded in 1798 in the campaigns of 1806, 1813 - 15 and 1870/71. The "Garde du Corps" regiment received a standard for each squadron. Therefore it existed in five specimen. In 1813, however, only one of these remained with the regiment. On January 29th, 1890 this was included in the stocks of the Royal Arsenal in Berlin. The fate of the other four standards of 1798 is recorded in the history of the "Garded Corps" regiment (by Graf von Brühl, Berlin, 1890; W. v. Schöning, Berlin 1840 and 1856).

The regimental standard, once of splendid appearance, is a double-leaf standard.

Originally 48 square cm, it shows the emblem of Frederick II in relief embroidery on a white silk lamé ground (2). The ground of the medallions on the emblem is orange. The metal threads (in weft) run vertically within the white ground, horizontally in the central medallion and diagonally in the corner medallions.

The density relations between basic and pattern weft and between ground and binding warp in white lamé has a ratio of 2 : 1. The orange ground lamé is more densely woven in the pattern weft, in a ratio of 1 : 1 between the ground and pattern weft.

The ground tissue has one canvas weave respectively. The pattern weft is tied off from the binding warp in the weft body. This lamé, together with an underlying dressed, loose raw linen forms the embroidery ground.

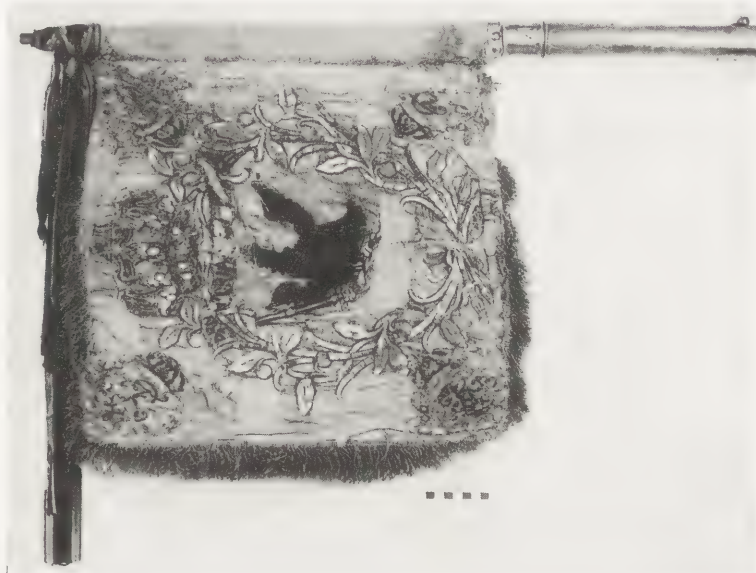


Fig. 2 The Frederician emblems of 1798

Fig. 1 The Prussian standard of the Garde du Corps regiment prior to restoration

Only the orange background of the corner medallions does not have an additional linen grounding in view of its low flexibility. The embroidery ground of each standard leaf consists of four layers of material in the middle, three at the corners and only two layers in the white area.

The embroidery ground is covered from the back side by the so-called "lining". This again consists of dressed and loose raw linen.

The double leaf standard of the cuirassier regiments was composed of altogether 8 - 12 layers of material. In addition there was the relief embroidery, the fringe and a pole of 3 m in length.

In the following details will be given concerning the colouring and design elements. In the soaring eagle the imitation of the plumage is embroidered in surface stitch, with black silk yarn. **The eagle, armed with a silver sword and thunderbolt, displays the letters "FWR" on its chest and wears a king's crown on its head.** A silver palm branch with a laurel branch with green leaves and red berries winding around it forms the framework of the central medallion. These branches are held together by a large golden bow.

The ribbon, on an orange ground, is inscribed with the golden letters "Pro Gloria et Patria".

The corner medallions depict the crowned golden signature, framed in by the palm and laurel branches.

The technique of the embroidery is known as "gold embroidery", with metal thread and a double yarn of silk, and tinsel web yarn. The metal thread are brass silvered and silver gilded, according to the laser microanalysis. The material used for the reinforcement of the relief embroidery are cardboard (0.4 - 2.0 mm) cloth, dense raw linen and silk yarn.



Fig. 3 The condition of the central ground of the medallion before restoration

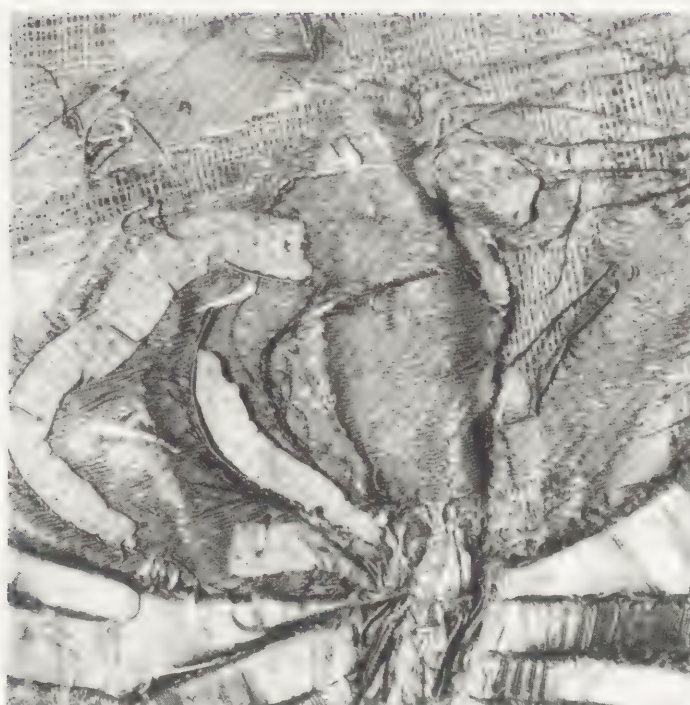


Fig. 4 Detail of the embroidery of the central medallion (sash) before restoration

Condition

The present condition is marked by two previous interventions - of the years 1813 and 1900 - and by damage caused during storage during the last war. The originally white ground was covered over a large area. This covering, with a cotton fabric now brown and brittle, in part also covered the central medallion. The cotton fabric was covered with remnants of tinsel web threads and a great deal of dust.

Uncovered parts of the embroidery ground revealed its fragmentary character: only a few places showed that the original material was a lamé. Pattern weft and connecting warp were almost completely disintegrated in the basic fabric. The linen underlying the lamé also showed small missing places, showing the white lamé layer underneath. Black remnants of embroidery showed under the microscope underneath the linen of the central medallion. These showed the extent of the destroyed embroidery of the tail and wing plumage (3). 30 per cent of the underlying fabric was bared or entirely missing (4). The metal embroidery was in part seriously damaged and gave the formerly silver and gold threads a black appearance due to the formation of silver sulphide.

Further fragments of the embroidery ground were found in the carefully considered removal of the cotton covering. All embroidery ground fragments show a greater or lesser degree of brownish discolouring.

The predominantly white missing parts found at the time of the removal of the cotton covering is explained by fibre damage in the stage of the manufacturing process of the white silk. Moreover the fluctuations of air humidity to which the standard had been exposed for almost two centuries caused other kinds of damage. The resulting changes in dimensions in the fibre, with the additional burden of the embroidery ground with the heavy embroidery led to a loss of elasticity and irreversible dilations. The mechanical stability of the fibre and its resistance to bending and tearing were reduced to an extent in which every movement led to further damage. The storage during the last war caused more recent damage, above all in the orange grounded parts.

The report on the condition of the object also includes the following facts: The embroidery ground on the side of the pole, with the leaf ending in the loop only showed a narrow deformed remnant. The interfacing, no longer the original, was uncovered. This interfacing is a dense raw linen reinforced by twisted yarn tissue and fine-drawn sewing of the imitation silver fabric.

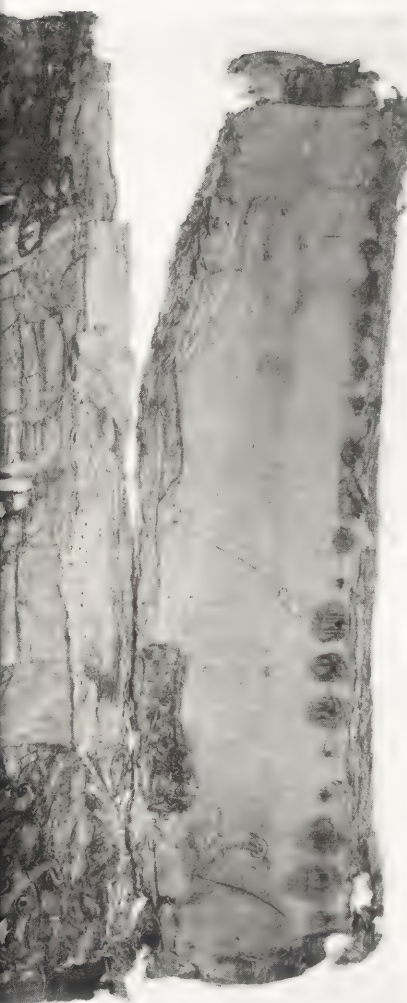


Fig. 5 Original loop, with the wedge-shaped missing part

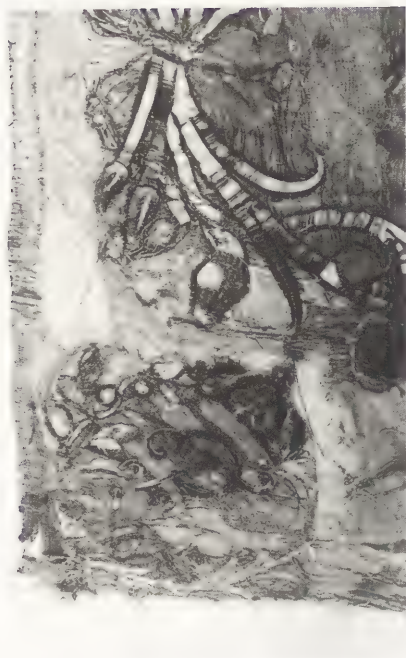


Fig. 6 Lower corner medallion of the pole-side

The loop covering the original had been repaired. Here as well the silvery tissue of the original ground had been imitated. Remnants of it were on the hems and in threads on the edges.

A braided plait of tinsel web threads and 40 cm of the remnants of a silver braid, a former nailing web were found sewn in and turned up in the longitudinal edge. The completed loop was nailed with an equilateral silk braid in the staggered cube design. The nails, iron pins with brass heads, had left large rust marks, now imprinted on the original loop. Apart from a remnant in the shape of a frame on the interface, the embroidery ground of the original loop was missing. The interfacing of the original loop consisted of dense raw linen reinforced by loose material. Since the loose raw linen was the same used to reinforce the lamé, it may be stated that this had been the original interfacing.

That loose linen belonging to the interfacing had become similar to gauze as a result of friction against the pole. It had several holes. A greenish discolouring was caused by the corroding brass shell of the pole.

At the top end of the interfacing of the loop, 11 cm in width, there was an attached diagonal dense raw linen stripe, folded six times. (Perhaps it had been intended to compensate for the narrowing of the pole.) 8 cm of the remnant of a silver braid, also a former nail band, was attached to it.

If the original loop and the standard leaf were unfolded, a wedge-shaped hole in the upper part of the corner medallion was clearly seen (5).

Research

The history of the Royal Prussian Garde du Corps Regiment proved to be of great importance for the successful restoration and conservation of the standard. Analyses of the material and techniques and of the historic background indicated a repair in 1813 and an extensive treatment around the turn of the century. The loop occupied a key position in this respect. The treatment undertaken was most clearly evident in this part. The small nail band remnant was identical with the nail holes of the inner row of nail holes. **It was the remnant of the original nail band, a silver braid in diamond design.** The nail holes closest to the leaf were in conformity with the remnant of 40 cm in length. It was the second nail band in diagonal cube design. The conclusion was drawn that the second nail band became necessary after the standard had been hit by a cannon ball in 1813, as reported in the history of the regiment. The embroidery ground, the interfacing, nail band and pole had been damaged. This was followed by a repair. The pole was covered with nickel silver plate, and the patching of the hole was stabilised with new nails. Remnants of sewing thread which were found could prove that the original nail band remnant had been used in the repair of the hole.

The silver braid mentioned could have served to cover the seam of the repair.

The report published in the regimental history on the kind of damage and the conclusions drawn from the investigations undertaken constitute a contradiction. The consequences of the cannon shot did not show in the lower part of the standard, but in the upper part. (This was proved by the wedge-shaped hole.) Nor was the leaf shortened, as asserted in the report, but it was merely separated from the loop. (This was indicated by the embroidery remnants between the lower corner medallion and the loop (5).)

As a result of the research the damage of 1813 could be clearly and reliably explained. Doubts arose in regard to the similar colouring of all five standards. (A complete explanation is excluded in view of the loss of three of the standards.) The present contribution proves that historical, art historical, material analytical and production technological investigations are essential prerequisites of a successful conservation/restoration.

The phase of conservation of ensigns introduced by the emperor Wilhelm II (1889-1918) could be regarded as the occasion for the extensive restorations around the year 1900. The standard was to be restored as a magnificent ensign. The double leaf standard was separated to this purpose, in order to exchange the damaged interfacing. The damaged embroidery ground was covered



Fig. 7 Fixed taffeta during lining

up with the fine cotton fabric (density: 36 warp and 38 weft threads/cm). Tinsel web threads drawn over it were intended as an imitation of the original silver fabric. The third nailing was fixed onto the completed loop, opposite the former nail holes. The pole, broken in several places received a brass shell. These measures will in the following be referred to as the "old restoration".

Measures

The task of the renewed conservation/restoration consisted in safeguarding the damaged parts against further destruction by means of reversible measures, making it into an aesthetic museum exhibit and historic testimony. To that purpose alterations were made in the old restoration.

Apart from the separation of the double leaf standard, the removal of the cotton covering represented the most significant operation.

The cotton covering of the central medallion was removed prior to the wet cleaning. This revealed that fragments of the original lamé ground were left under this covering. This encouraged us to attempt the complete removal of the cotton covering after the successful cleaning operation. Removal was no problem for the cotton covering on the outlines of the flying side of the standard, but not so for the cotton covering reaching far below the embroidery. In those parts the covering either **had to be cut off or left intact. The cutting was affected along** the large crown outline. The cotton covering on the pole side was left untouched. (There the embroidery ground only remained in the deformed strip.) On the one hand the cotton covering is a substitute stabiliser for the missing parts of the embroidery ground, on the other it is documentary evidence of the old restoration of the original. In addition the tacked seam on the lower edge of the leaf had to be undone. The embroidery ground, dilated in that place, had been drawn up by the tacked seam of the hems of the shorter interfacing, which caused a compression. In consequence a few attachment stitches in the lower right corner medallion also had to be undone. This loosened the tension in the embroidery ground and straightened out the lower edge of the leaf. The corner medallion was lowered by 2 cm (6). The extensive missing parts had in part to be reinforced, in order to stabilise the torn tissue and broken threads in the damaged embroidery ground. A taffeta fabric, selected for this, was well adapted to the original material in warping density and weft rib thickness. Various factors had to be considered in connection with dyeing: assimilation of the colouring to the brownish fragment surfaces would result in a tone-in tone colouring, regardless whether the original had been orange or white. That is why a colouring was selected for the outlines of the fragments which allowed an approximate recognition of the original. The extent of

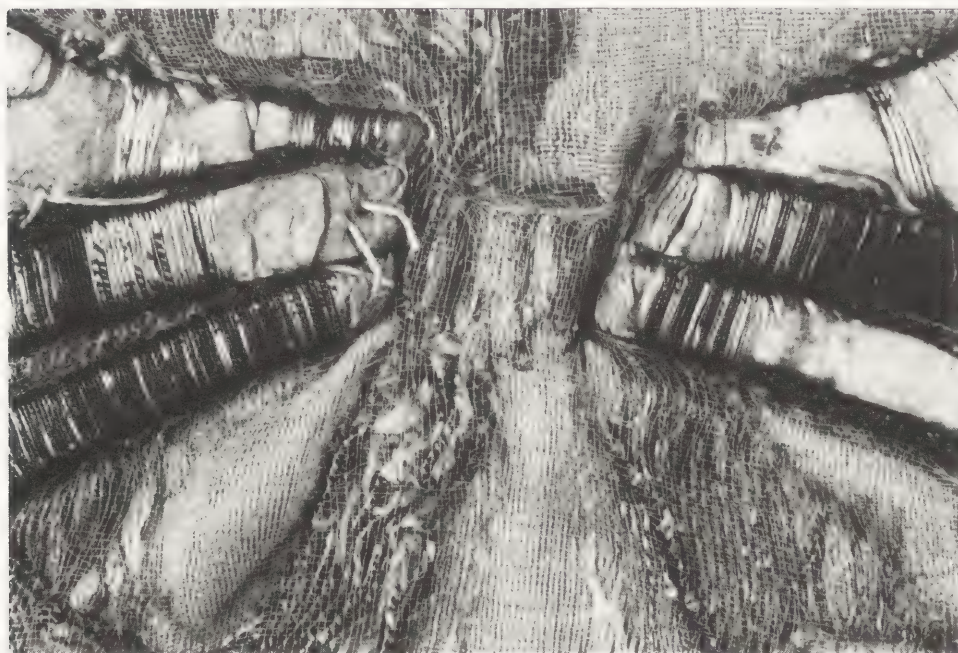


Fig. 8 Taffeta lining with crepeline covering: detail

the missing parts allowed for the unity between the contrast of the colour of the fragment areas and the dyed restoration material. The advantage of this colouring consisted in the recovered vivacity of the general impression of the standard.

The dyed taffeta lining was fixed in large areas, covering several missing parts, so that the ground should not lose its cohesion.

The stabilising material, carefully inserted under the fragments was fixed with the finest insect needles. This was essential, because the silk fragments, partly pulled out of shape, were hard to fit in with the run of the threads (7). Tinsel threads of the silver fabric imitation which blocked access in the process of stabilisation were loosened on one side and subsequently re-fastened. In sewing great care was taken not to stitch more than absolutely necessary into the brittle fragments. This was facilitated by an additional covering of the areas with crepeline (8).

That covering also serves as surface protection. It was laid over the entire ground and rolled in and fixed along the edges and around the embroidery. The unstable veil tissue had to be treated with a stabiliser to allow this application of crepeline. Polyacrylic acid ester (D 320) was used in a ratio of 1 : 10. It should be underlined that this substance is not adhesive in this solution; it only stabilises the fabric and makes the restoration reversible.

In the treatment of the ground specific requirements had to be considered for the pole side. The weight of the standard and the loop will have to be held by the pole. This calls for a method of attachment which can be placed under tension. Since the loop was originally formed by the extension of the restoration material had to pass seamlessly into the loop over the whole length of the pole side. These requirements were complied with by cutting into the taffeta, otherwise applied in one piece. The top corner medallion could be detached due to the advanced degradation of the embroidery ground.

The corner medallions, each in a different stage of degradation, also required the greatest care in covering the missing parts. A crepeline covering could not be applied, since omission and covering would have been unfavourable. Where necessary treatment of the fragment outlines with tie and lining stitches this proved adequate for stabilising the ground. The same also applied to the inscription ribbon.

Coverage of the white ground with crepeline concluded the restoration of the silk ground. The edges of the ground of the corner medallions not covered with crepeline could be stabilised at the same time. The absence of the crepeline was unimportant, since the inscription and the corner medallions represented separate design elements.

The object of restoration work, namely the recognition and conservation of an exhibit in its historical originality was achieved with the greatest precision (9).



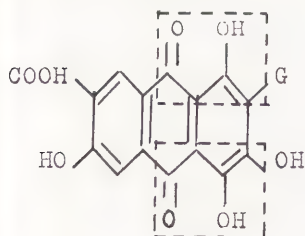
Fig. 9 Total view of the leaf after restoration of the silk ground

ABSTRACT

This paper describes the structure and properties of the cochineal dyestuff of carmine acid (CA). It considers possible ways of CA combining with silk in the form of mordant, direct and acid dyes, and undesirable side reactions of CA resulting in the formation of insoluble compounds, when CA is extracted from cochineal and silk is dyed in the extract are presented. The 17-19th century dyeing recipes were analysed. Methods of an experimental investigation of the CA extraction and silk dyeing processes, and of assessing the results and quality of dyeing models and genuine 17-19 century textiles.

KEYWORDS

Cochineal; quality of dyeing; interaction between silk fibroin and carminic acid in forms direct, acid and mordanted dyes; insoluble complexes of carminic acid; analysis carminic acid and mordanted cations in solutions and the dyed silic; spectrophotometry; spectrofluorimetry.



--- fragments capable of producing chelate complexes with metal cations
G - glucose

Fig.1 Carminic acid

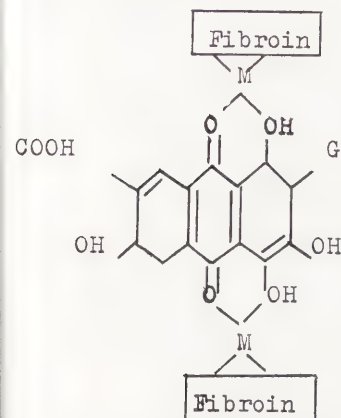


Fig.2 An assumed structure of "lac"

M - cation of metal

TECHNOLOGY OF DYEING SILK BY COCHINEAL. PART 1. THEORETICAL ANALYSIS OF THE PROBLEM AND DEVELOPMENT OF INVESTIGATION METHODS

V.P. Golikov
VNIIR
10 Krestyanskaya Pl.
Moscow, USSR

Introduction

This paper is the first of a series of publications devoted to a detailed investigation of the technology of dyeing silk by cochineal, a main red dye raw material in the 16-19 centuries. This investigation is being conducted for the SNRPM-2* of the V/O "Soyuzrestavratsia" with a view to the recreation of the technology of dyeing textile fibres by natural dyestuffs.

Properties of Cochineal

Cochineal, the dried bodies of female cochineal insects *Dactylopius coccus* feeding on *Opuntia cactus* found in Central and South America (1).

Aztecs and Incas in pre-Columbian America used cochineal for dyeing purposes. Right after America had been discovered in the late 15th century, it began to be exported to Europe, and in the late 16th century it became a basic red dye in the production of highly artistic textiles at medieval textile mills (2).

Cochineal contains 10-15% of red anthraquinone water soluble dye of carminic acid (CA). This dyestuff, along with its analogue, kermesic acid, is contained in other insects of the suborder Coccinea which preceded cochineal being commonly used for dyeing (1, 2).

CA, like most natural dyestuffs, has several specific properties which distinguish it from synthetic dyes.

1. In modern synthetic dyes an attempt is made to create 1 type of functional groups capable of combining with fibres. It simplifies the dyeing procedure and standardizes results. CA contains several types of functional groups which interact differently with silk fibroin. CA is considered a classical mordant dyestuff since it contains fragments capable of producing chelate complexes with metal cations. If, before dyeing, silk is mordanted (processed with salts of mordant cations), CA produces with silk a strong "lac", the triple insoluble chelate complex "CA - mordant cation - fibroin" (Fig. 2).

The formation of "lac" causes a long-wave shift in CA maximum absorption and increases its intensity, with colour characteristics depending upon the nature of a mordant cation. CA light fastness in "lac" is much higher than in the free form.

CA, however, can dye silk not only as a mordant dyestuff. Owing to intermolecular interactions of $-OH$ and $>C=O$ polar groups CA, in the free form or in the form of a soluble salt can combine with fibroin as a direct dyestuff. In addition, owing to the groups $-COOH$ in the form of $-COO^-$, CA can interact with the basic groups of fibroin $-NH_2$ and NH in the form of $-NH_3^+$ and NH_2^+ as an acid dye forming ion bonds. This is possible with pH when² acid groups in CA and basic groups in fibroin are simultaneously, but oppositely charged, i.e., with $pK_1 < pH < pK_2$, pK_2 where pK_1 , pK_2 and pK_3 are respectively ionization constants of³ the groups $-COO^-$ of CA, NH_3^+ , NH_2^+ of fibroin.

2. In modern synthetic dyes, the aim is to separate the chromophore system and the functional groups, responsible for binding with, fibres in order to standardize dyeing results. By contrast, all the above-described types of functional groups in CA are closely linked to the chromophore system of the dye**. The-

* Special scientific research and production workshop which re-creates scientifically reliable highly artistic 17-19th century textiles for restoring palace interior decoration. It seeks to use the same natural dyestuffs used in genuine textiles.

** It is an inevitable price for the fact that man had to use for dyeing fibres compounds created by nature for other purposes.

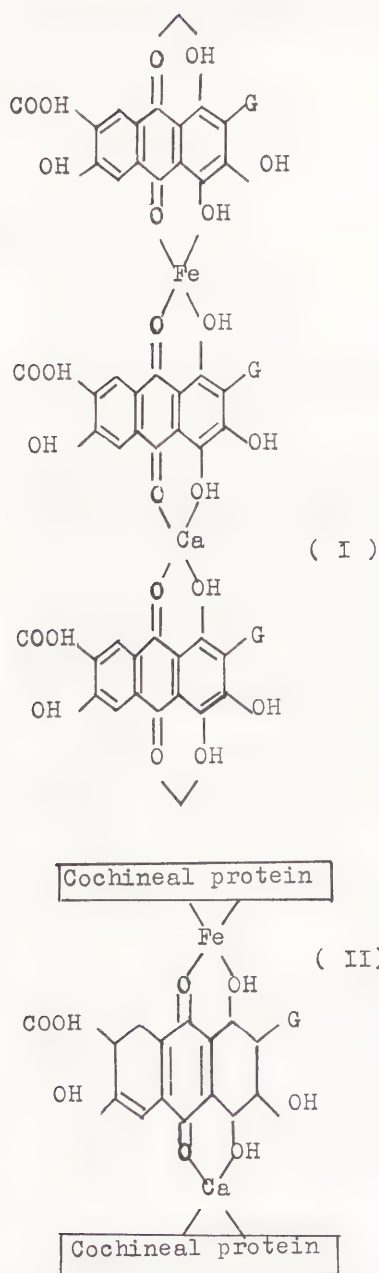


Fig.3 An assumed structure of insoluble complexes of carminic acid /CA/ in dye solutions: I - CA + cations; II - CA + cations + cochineal protein

refore, colour characteristics, light fastness and stability towards wet processing will not be the same for each of the above-described ways of CA combining with fibroin. The best quality dyeing is produced by CA in the form of a mordant, the worst, in the form of a direct dye.

3. CA contains 2 chelate fragments. Therefore, with metal cations present, CA is capable of producing insoluble multinuclear chelate complexes (I) in solutions (see Fig. 3). In cochineal itself CA is combined with different components of insect cells. When extracting CA, these components, e.g., proteins, can be extracted along with the dye and produce insoluble compounds (II) in a dye solution (see Fig. 3). Naturally, these side processes decrease the concentration of free CA capable of combining with silk, which is most undesirable.

Because of the above-described properties the dyeing of silk by cochineal is a very difficult and complicated process, and its results can hardly be re-created. The principal problems, which are necessary to solve in dyeing by cochineal, can be summarized as follows:

1. Ensuring the prevailing combination of CA in the form of "lac" with the necessary mordant cations, and preventing undesirable cations from participating in "lac".
2. Preventing the interaction of CA with silk in the form of direct and acid dyes.
3. Preventing undesirable side processes from forming insoluble combinations (I) and (II) when CA is being extracted from cochineal and mordanted silk is being dyed.

Analysis of Dyeing Recipes

Magnificent museum textiles, dyed by kermes and cochineal, show that skilled dyers solved this problem. At first sight it seems evident that these solutions can be found in old dyeing recipes. No doubt, these recipes describe important technological details. When dyeing silk in accordance with 18th century recipes, however, we failed to obtain dye wools close to textiles of that period. As was shown by an analysis of over 50 recipes (3-5), there can be several possible reasons for this failure.

1. In different recipes, sets of materials and procedures differ considerably. That is why it is difficult to differentiate between important and unimportant ones.
2. Different values are indicated in different recipes for one and the same technological factor. That is why it is not clear which of them are most important.
3. There is no evidence that skilled dyers actually dyed in accordance with these recipes. The authors of recipes written down in the 18-19th centuries, were, as a rule, not dyers, but rich and educated dilettantes. Influenced by fashion in the period of Enlightenment and French encyclopaedists, these people went for studying crafts and published books of recipes in the 18-19th centuries. Serious doubts arise, however, that these recipes contain a precise description of the dyeing technology: first, the authors of recipes did not carry out dyeing themselves; second, they could have failed to write down details that were self-evident at that time; third, dyers always kept their skill secret most carefully.

4. The same materials, in the 20th and 18th centuries, can be very different in the composition and properties, while the same terms can denote different materials.

Experimental Investigation of Dyeing Technology

In order to find out how the above-said technological problems had been solved, it was necessary to conduct an investigation of genuine 17-19th century textiles, as well as of model dyeings produced in accordance with the formulas. In order to assess the results and quality of dyeing a study was made of mechanisms of CA combining with silk, colour characteristics of dyeings and composition of mordant cations.

The following methods were applied to analyze the results and processes of dyeing silk by cochineal.

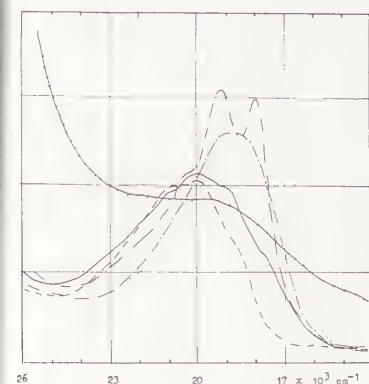


Fig. 4 Absorption spectra of aqueous solutions of carminic acid (CA)

1 - 3 - pure CA
1 - pH = 5,6
2 - pH = 2
3 - pH = 11
4 - 6 - CA + salts of different cations
4 - Al^{3+}
5 - Mg^{2+}
6 - Fe^{3+}

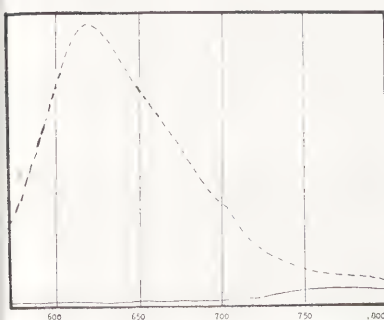
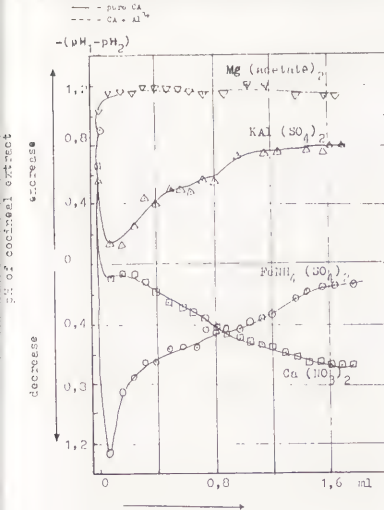


Fig. 5 Spectra of fluorescence of aqueous solutions of carminic acid (CA)



Volume of the 0.01 M solution of mordant salts, added to 15 ml of carminic acid.

Fig. 6 Dependence of pH of cochineal extract on the amount of mordant salt added
 pH_2 - pH of the cochineal extract with salts added
 pH_1 - pH of the control pure water with salts added

Qualitative and quantitative analysis of dyestuffs. CA, like other probable dyes used for toning, as well as tanning substances and cream of tartar were isolated from fibres by the technique developed earlier (6). CA and other dyes were identified by a spectrophotometric method, tannin and cream of tartar, by a thin-layer chromatography method on "Sulufol" plates in the systems "Chloroform: butanol: acetic acid: dimethylformamide" (20:20:5:8) and "butanol: acetic acid: water" (40:12:28). The quantitative analysis of CA was made by the spectrophotometric method. The CA content in extracts before, during and after dyeing was determined in the presence of KOH by the maximum of $17.3 \times 10^3 \text{ cm}^{-1}$ (578 nm). With alkali pH spectra intensity is much higher, insoluble complexes are solved, and the form of spectra depends little upon the composition of cations.

The quantitative analysis of CA in silk was conducted by the spectrophotometric method by the maximum of $18.3 \times 10^3 \text{ cm}^{-1}$ in a sulphuric acid extract. The sample was first dissolved in sulphuric acid. CA and silk are fully solved and all the CA complexes with cations are broken in it. CA is stable in sulphuric acid for several hours, produces intensive spectra with a well-defined structure, and the presence of silk and metal cations does not hinder the determination of CA.

The spectrophotometric determination of CA is made from the calibration curve of optical density versus CA concentration. Pure CA is required to determine it. To do so, CA, isolated from cochineal water extracts, was purified by means of column chromatography from highly molecular components of cochineal on "Sefadex" 6-15, and from cations, on the cation-exchange material "CU-2-8".

Investigation of Carminic Acid (CA)

Interaction in Solutions. Complex combinations of CA with metal cations were studied by several independent methods. The formation of complexes is accompanied by a sharp change in the electron structure of CA. That is why spectrophotometry and spectrofluorimetry proved to be the most efficient methods of investigating these processes.

Fig. 4 shows absorption spectra of free CA, its complexes with cations, as well as the formations of undesirable complexes of CA with cation Fe^{3+} of a dirty violet colour in water-pipe water.

One can see in Fig. 5 that Al^{3+} makes an intensively fluorescent complex with CA.

If α -hydroxyls of CA take part in chelate complexes, cations force out ions H^+ from α -hydroxyls during the formation of such complexes, which is accompanied by a decrease in pH of the CA solution. Potentiometric titration makes it possible to record this process (Fig. 6).

It is possible to determine the structure of the complex and to identify substituents taking a direct part in CA complexes with cations by NMR and infra-red spectroscopy methods.

Ionized and unionized forms of CA can be determined by the spectrometrical method or visually as CA is a pH-indicator. With acid pH = 3.5, water CA solutions are of orange colour due to unionized forms. With alkali pH = 9.5 the colour is violet due to the ionization of $-COOH$ and $-OH$ groups and the formation of salts and phenolate - ions (see Fig. 4). A mixture of these forms is present in the CA solution with pH = 7.

An analysis of the mechanism of carminic acid combining with silk fibroin was made by means of a set of agents selectively breaking different types of the dye combining with silk, and extracting dyes from silk after the combination had been broken*.

The total concentration of CA was measured in samples of dyed silk. CA was then isolated, which was combined with silk in the form of direct dyes. To do so, silk was treated with one of the agents breaking the intermolecular interactions of CA and fibroin: with dimethylformamide, pyridine, a mixture of ethanol: water (1:1), 8M urea solution in water. The sample was then treated in alkali aqueous solutions (pH = 10 - 11) so that all

* 2-5 mg. of silk are required for this investigation.

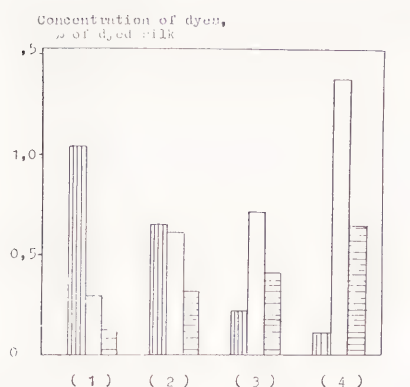


Fig. 7 Distribution histograms of carminic acid (1-3) and orcein (4) in the form of mordanted, direct, and acid dyes in dyed silk

(1) - crimson threads of 18 century three-coloured silk mordanted
(2) - crimson 18 century brocade
(3) - crimson 19 century polychrome silk
(4) - red-brown threads of 18 century polychrome silk

Legend:
 [hatched] - mordanted
 [white] - direct
 [horizontal lines] - acid

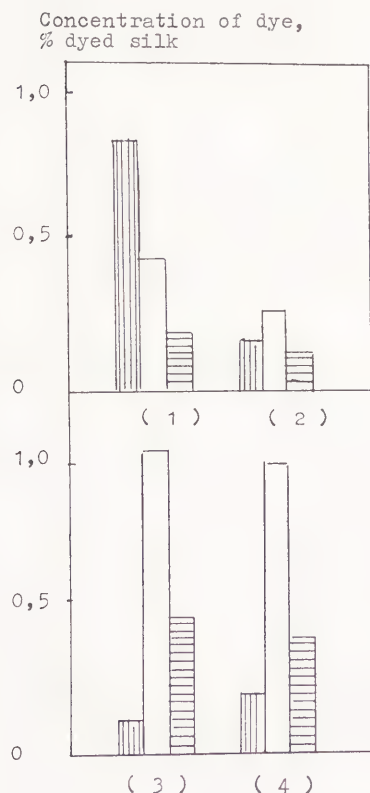


Fig. 8 Distribution histograms of carminic acid and orcein in the forms of mordanted, direct, and acid dyes in model dyed silk

(1), (2) - carminic acid;
(3), (4) - orcein.
Silk is mordanted with salts of Al^{3+} (1, 3) and Ca^{2+} (2, 4).

Legend:
 [hatched] - mordanted
 [white] - direct
 [horizontal lines] - acid

$-NH_3^+$ and $>NH_3^+$ fibroin groups might turn into the $-NH_2$ and $>NH_2$ form, and this breaks up their combination with CA^{2-} in the form of acid dyes.

Dyes combined in the form of "lac" remain in silk after these two procedures. In order to separate "lacs" by strength they are first treated in 0.1 HCl. After that CA combined with silk in the form of "superstrong" complexes remain in 17-19th century textiles. They break up only in solutions of H_6ntph and H_5dtpa complexons.

In order to determine the efficiency of the above-said agents a study was made of desorption kinetics of CA from silk under their effect. An analysis of kinetics showed that 40 minutes at 70°C will suffice to break up any types of CA combination with fibroin by means of appropriate agents.

By measuring the quantity of CA isolated from silk under the effect of appropriate agents, it is possible to make a histogram of CA distribution by combination mechanisms for each sample. Such a histogram characterizes objectively the result and quality of dyeing: evidently, the more of CA is combined in the form of "lac", the higher the quality, and vice versa, the more of CA in the form of direct dyes, the worse the quality.

As was shown by an analysis of histograms, 17-19th century museum silk textiles differ rather substantially by the quality of dyeings (see Fig. 7).

For comparison, Fig. 7 shows histograms of the 18th century red textile dyed by orcein. This dyestuff contains no fragments capable of producing strong chelate complexes. As can be seen from the histogram in Fig. 7, direct dyes prevail in this textile.

Fig. 8. shows also histograms of silk model dyed by cochineal and orcein, after having been mordanted by Al^{3+} and Ca^{2+} salts. As can be seen from the histograms, these samples differ considerably both by the total content of dyes and by their distribution.

Analysis of Mordant Cations. Samples of the 17-19th century textiles were first cleaned of impurities containing metal cations. Mineral dust sticking to lipid impurities was removed by perchlorethylene (PChE) with 0.1% aqueous non-ionogenic detergent solution added. Such a mixture does not dissolve CA in silk. The sample, split into fibres to increase the surface, was rotated in a vessel with PChE by a magnetic mixer for 24 hours. Water-soluble impurities were removed in the same way in distilled water.

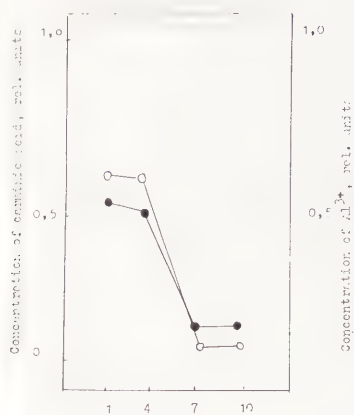
The total cations content can be measured by any elementary analysis method. In this investigation X-ray fluorescence was employed for large samples, and a laser emission spectral microanalysis for microsamples. CA in the form of direct and acid dyes was first removed from silk in order to determine selectively mordant cations linked to CA and fibroin in the form of "lac". The sample was then treated with H_6ntph and H_5dtpa complexons with high stability constants. With pH = 1-4 they break mainly complexes of trivalent cations (Al^{3+} , Fe^{3+}), and with alkali pH = 8-10, complexes of bivalent cations (Ca^{2+} , Mg^{2+} , Fe^{2+} , Pb^{2+}).

It is evident that after "lac" has been broken, CA and mordant cations will be simultaneously released from silk. Therefore, those cations can be regarded as mordant, whose release dynamics correlates with CA extraction dynamics when the complexon solution pH is changed. As can be seen from Fig. 9, Al^{3+} is a mordant cation in the 18 century textile samples that were studied.

Colour Characteristics Analysis

Data on colour characteristics is necessary for an objective assessment of the results and quality of dyeing. They were assessed by the diffuse reflection spectra.

The standard colour characteristics X, Y, or Z can be calculated from these spectra by the appropriate technique. They can be assessed approximately by the spectra structure. CA absorption spectra can be studied right in the silk by the diffuse reflection spectra. As can be seen from Fig. 10, the position of maxi-



pH of the complexon solution

Fig. 9 Dependence of the extraction of carminic acid and Al^{3+} from dyed silk on pH of complexon solution, destroyed "Lac". It was studied crimson threads of 18th century three-coloured silk. Direct forms of carminic acid were removed in advance.

● - carminic acid
○ - Al^{3+}

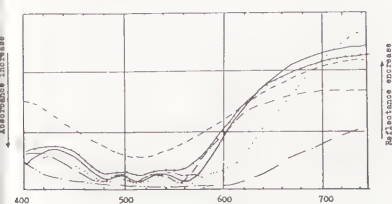


Fig. 10 Reflectance spectra of silk, dyed with cochineal

1 — crimson threads of three-coloured 18th century silk
2 - 6 — model samples
7 — without mordanting
8 - 10 — silk is mordanted with salts of different cations
3 — Al^{3+} ; 4 — Sn^{2+} ; 5 — Fe^{3+} ; 6 — Cu^{2+}
7 — Al^{3+} + dyeing in presence of cream of tartar

mums and their width enables one to determine the most important technological details of dyeing: the type of the principal mordant cation (Al^{3+} or Sn^{2+}), the correlation of CA in the form of "lac" and direct dyes, to find whether galls and cream of tartar were used.

Conclusion

1. To dye silk with cochineal it is necessary to combine the silk fibroin and carminic acid in form of red chelate complexes and to prevent side reactions: interaction the fibroin in forms of complexes with undesirable cations, acid and direct dyes; formation of insoluble complexes during extractions and dyeing solutions.

2. To indicate the success of dyeing it is necessary to assess the quality of the dyed silk. It is possible to do, measuring the quantity of carminic acid, combined with fibroin in forms mordanted direct and acid dyes and investigating a nature of the chelate complexes of carminic acid in the dyed silk.

3. To study the processes of dyeing and quality of the dyed silk it is possible to apply a complex of experimental techniques, including the special agents, selectively destroying interactions between the silk fibroin and mordanted, direct and acid forms of carminic acid; spectrophotometry; spectrofluorimetry; potentiometric titration; elementary analysis of cations.

References

1. Baran F.L.C. Cochineal carmin: an ancient dye with a modern role. *Endeavour*, New series Volume, 2, No. 2, 1978, 85-92.
2. Hofenk de Graaf J.H. Natural dyestuffs for textile materials. Origin. Chemical constitution. Identification. ICOM. - Amsterdam, 1969.
3. Levshin V. Full dyer. Department 3, part 2. Sanct Petersburg, 1819.
4. Regan P. New book for dyers. Moscow University Typografy, 1794.
5. Agentov M. Revelation of hidden arts, Moscow University Typografy, 1769.
6. Golikov V.P. Spectrophotometric Determination of red and violet dyes in museum textiles. ICOM. - Sydney, 1987.

ABSTRACT

Classification scheme was developed, pertaining to the dyeing technology: the set and number of colours; the composition of dyes in threads of each colour; the number of shades of each colour; the extent to which one dye was used to obtain different colours and shades; characteristic combinations of dyes; the degree of colour homogeneity of filaments in threads; the dye content in % per 100 g. of silk; the size and distribution of indigo particles in the volume and on the surface of filaments.

A study of the collection of well documented textiles from the collection of Moscow Kremlin State Museums was begun by means of this system. A comparative study of 9 Persian and 7 Turkish 16-17th century textiles was carried out.

KEYWORDS

Medieval Turkish and Persian textiles; characteristics of the dyeing technology.

A COMPARATIVE STUDY OF DYEING TECHNOLOGY IN 16-17TH CENTURY PERSIAN AND TURKISH TEXTILES FROM MOSCOW KREMLIN COLLECTION

V.P.Golikov, I.I.Vishnevskaya
VNIIR
10 Krestyanskaya Pl.
Moscow, USSR

Introduction

This paper endeavours to develop a classification scheme pertaining to the technology of dyeing textile fibres, and use it for a comparative study of Persian and Turkish textiles. By means of such a classification scheme in combination with data on the style characteristics and the technology of weaving, it is possible to carry out attribution and dating of museum textiles more reliably and objectively.

It is necessary to develop a system of technological characteristics on the basis of a first-class textile collection reliably dated and attributed by independent methods. It is such textiles that form the basis of the collection in Moscow Kremlin State Museums (MKSM).

In the 16-17th centuries Russia maintained close contacts with Oriental countries. Precious textiles were traditional gifts from trade and diplomatic missions to the Russian Czar. Afterwards these textiles were passed over to the Church to be used in making clothes and church-plate. That is why the history of textiles of that period in the MKSM collection has been thoroughly documented from the time they came to the Czar's Treasury till the present time. 9 Persian and 7 Turkish textiles, and for comparison 2 Chinese and 3 Italian textiles were studied at the initial stage.

Persian Textiles

1. Metropolitan Alexis' sticharion, 14th century.
2. Chasuble, N 10325, late 16th century.
3. Cloak, N 10195, middle, 17th century.
4. Cut velvet, N 36815, middle and border, 17th century.
5. Cloak, N 10199, 17th century.
6. Cloak, N 6710, border, 17th century.
7. Cloak, N 10194, the first half of the 17th century.
8. Joseph's (Job's) sack-cloth, middle, 17th century.
9. Violet velvet, 18th century.

Turkish Textiles

10. Prince Skopin Shuisky's pall, border, late 16th - early 17th century.
11. Sticharion N 13107, basic textile of late 16th century (Bursa).
12. Sticharion N 13107, patch, late 16th century.
13. Cloak N 10195, border, 17th century.
14. Sleeves without a number, 17th century (Bursa).
15. Cloak N 10194, border, 17th century.
16. Joseph's (Job's) sack-cloth, 17th century.

Several textiles of the same period from other countries were studied for comparison.

Chinese Textiles

17. Horse-cloth N 10556 imported by Spafarius, 17 century.
18. Two-coloured black and green damask, 17th century.

Italian Textiles

19. Sticharion N 13107, skirt, 17th century.
20. Prince Skopin Shuisky's pall, border, late 16th - early 17 century.
21. Cloak N 10199, border, 17th century.

Study Technique

The composition of dyes was studied in extracts by means of spectrophotometry, spectrofluorimetry and thin-layer chromatography. Dyes were extracted from microsamples of dyed fibres, by a special set of agents selectively breaking different types of the connections of dyes with fibres by means of the technique

Fig. 1 Distribution of the number of colour (N), kinds of dyes (M) and their relation (M/N) in polychrom Persian and Turkish textiles (N), (M) and (M/N) - relation of the numbers of textiles with given (N), (M) and (M/N) to the total number of textiles of each country.

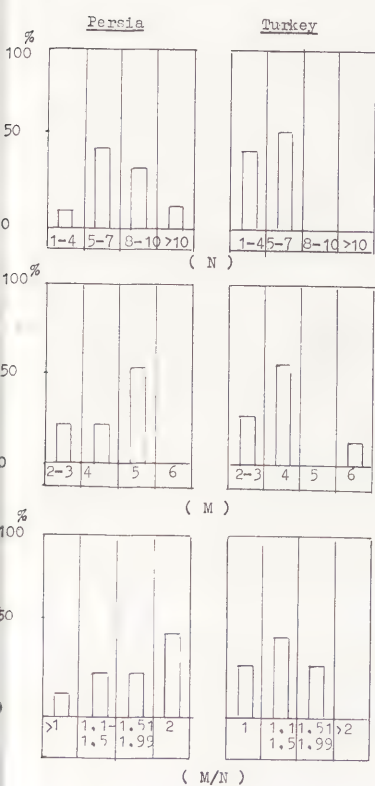
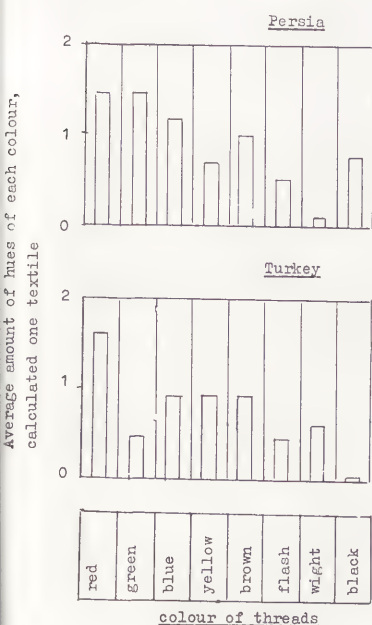


Fig. 2 Distribution of hues of each colour for the studied Persian and Turkish textiles.



worked out beforehand (1). This made it possible, firstly, to extract dyes in soft conditions and, secondly, to extract consecutively and selectively vat, direct and mordant dyestuffs from green, grey and violet fibres dyed by several dyestuffs.

A quantitative analysis of dyestuffs was made in extracts by a spectrophotometric method.

The composition of cations was studied on microsamples cleaned beforehand by means of an emission spectral laser microanalysis. The composition of mordant cations was calculated by comparing dyed and undyed threads in one textile.

Depending upon the technological type of a dyestuff (vat or mordant dyestuff), and also upon how textile raw material was dyed: in the form of fibres, spun threads or a ready-made textile, the dyestuff can be variously distributed in the textile structure, between threads in the textile, between filaments in the thread, as well as on the surface and in the volume of separate filaments. These characteristics were determined in reflected light at 20-400 \times magnification and in transmitted polarized light at 360-500 \times magnification.

In polarized light, by the pleochroism effect, it is possible to make a preliminary identification of dyestuffs with asymmetric carbon atoms capable of rotating the light polarization plane (carminic acid, alkanin and shikonin).

Experimental Results

A system of technological characteristics pertaining to the dyeing technology, as well as the first results of its application for comparing the 16-17th century Turkish and Persian textiles is described below.

The first group includes 3 interconnected technological characteristics for which both average values and histograms of distributing textiles by these characteristics were determined (see Fig. 1).

The number of kinds of dye raw materials (M). The average values of M are close for the Turkish and Persian, as well as for the Italian and Chinese textiles, and constitute 4. In the Turkish textiles, however, ones with M = 4 prevail, whereas in Persian textiles, ones with M = 5 (Fig. 1).

The number of colours (N). The average values for the Turkish textiles constitute 5, 25, for the Persian ones, 6, 9. The difference of the distribution on N between them is even greater: among the Turkish ones, textiles with N = 4 - 5 prevail, there are no textiles with N = 7, whereas among the Persian ones there are more textiles with N = 7 - 10, and there are textiles with N = 12 - 13 (Fig. 1).

N/M relation. The value of N/M is in fact an 'average coeff' of the use of dye raw material which shows approximately how many colours and shades dyes could or would obtain from one kind of dye raw material. Textiles with N/M \approx 1 are typical of the Turkish ones, and textiles with N/M \geq 2 are characteristic of the Persian ones (Fig. 1). It could mean that Persian masters dyed in one dye solution two or more times, which raised the efficiency of using dye raw material and the coloristic variety of dyed fibres.

The number of shades of each colour P(i). Each P(i) and $\sum P(i)$ characterize respectively the variety of individual colours and the textile as a whole (Fig. 2).

The values of P(i) for red, yellow, brown and grey threads in the Turkish and Persian textiles are comparable and constitute about 1.5. In green threads of the Persian textiles P(green) = 1.5, whereas in the Turkish ones it is nearly half that: P(green) \approx 0.8. In blue threads of the Turkish textiles values of P(blue) constitute 0.86, in the Persian ones, 1.2. It means that the number of green and blue shades in the Persian textiles is greater than in the Turkish ones.

Particularly characteristic is the difference in black and white threads. Nearly in each Persian textile there were black threads, whereas they have not been so far found in a single Turkish textile studied.

Purely white threads were often used in the Turkish textiles, whereas in the Persian ones there are almost no purely white threads, threads toned in flesh colour were used in their stead.

The set of dyes in threads of different colours. Different shades of each colour can be obtained by two principal methods: (1) Dyeing threads simultaneously or consecutively by several dyestuffs. In this case the number of dyestuffs required is less, but the dyeing technology is more complicated. (2) Using separate dyestuffs for each shade. In this case the number of dyes, as compared to method (1), necessary to obtain the same number of shades rises, but the dyeing technology is simpler.

Method (2) was applied to obtain different shades of red colour in the Persian and Turkish textiles. An exception seems to be warm pink and orange pink threads in which, in addition to carthamine (safflower red dye), we found another, so far unidentified, yellow brown dye. Its nature can be interpreted in different ways: (a) a separate, specially added, second dye; (b) an admixture of another, yellow, dye from safflower petals which remained in carthamine due to insufficient purification; (c) a product of photochemical degradation of carthamine. The third suggestion is confirmed by the fact that in threads on the other (wrong) side, where textile was not subjected to the effect of light, the content of the second dye is much less than on the face side of textile.

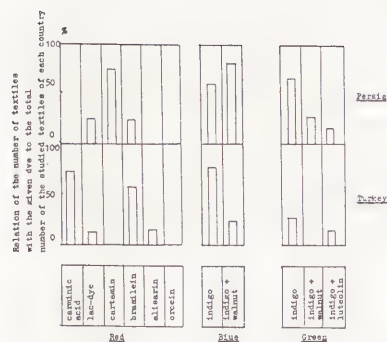


Fig. 3 Frequencies of the application of different dyes in polychrome Persian and Turkish textiles

In the Persian textiles the most common dyestuff is safflower carthamine. We found also lac-dye of *Laccifer lacca* and brazilin of redwood (brazilwood). The latter dye is commonly found on the other side in threads mixed with pink threads dyed by safflower. Redwood was probably used as a cheap substitute of safflower (Fig. 3). In red threads of the Persian textiles we have so far failed to find common dyestuffs of kermes, cochineal, madder and orcein (Fig. 3).

In the Turkish textiles the principal red dyestuff is carminic acid of cochineal or kermes. Brazilin can also be found, though not on the face but on the other side. In textile (N 16) lac-dye and alizarin of madder* were found. Carthamine, so characteristic of red Persian textiles, has not yet been found in the Turkish textiles (Fig. 3).

Thus, red threads in the Turkish textiles differ, by the composition of dyestuffs, from the Persian ones by two characteristics: the presence of carminic acid and the absence of carthamine. This predetermines coloristic differences: intensive crimson shades prevail in the Turkish textiles, whereas in the Persian ones, delicate pink shades of the red colour.

In the textiles studied blue threads were dyed by two different methods: either by a pure indigo, or indigo and yellow brown walnut dyestuffs** of walnut shell. The first method produces pure blue or sky-blue shades, the second one makes it possible to obtain complex shades of grey blue colour (Fig. 3).

Blue threads prevail in the Turkish textiles, dyed by the first method. In the Persian ones the second method was applied more often, with a different correlation of indigo and walnut dyestuffs (Fig. 3).

Green threads in the textiles were obtained by different methods: (1) dyeing by indigo and yellow luteolin dyestuffs; (2) dyeing by indigo and yellow brown walnut***; (3) dyeing by indigo, walnut and luteolin.

Method (1) prevails in green threads of the Persian textiles. (2) and (3) were found also. Method (3) has not been detected in the Turkish textiles, only (1) and (2) were found (Fig. 3).

Luteolin prevails greatly in green threads of the Persian textiles, whereas in the Turkish textiles various yellow dyestuffs

* These data confirmed doubts as to textile N 16 belonging to Turkish textiles.

** Mixture of tanids and juglon.

*** Like method (2) of dyeing blue threads, but in green threads there is more walnut dyestuffs than in blue ones.

were found, including luteolin, walnut and as yet unidentified dyestuffs (Fig. 3).

Walnut dyestuffs was found in flesh-coloured threads with different shades and intensity. Fibres could have been toned by walnut either for aesthetic reasons, or to increase the durability of fibres, as walnut dyestuffs is a very strong biocide.

Flesh-coloured fibres are found primarily in the Persian textiles, whereas white, untuned, threads prevail in the Turkish ones (Fig. 3).

Black threads are absent in the Turkish textiles and are found in almost all the Persian ones. In the textiles studied we found two methods of dyeing in black colour: (1) dyeing fibres, mordanted with ferrous salts, by catechin-containing, which produces a black colour with a brown shade; (2) the same dyeing as in method (1) + additional dyeing by indigo, which produces a deep black colour.

Method (1) is applied in most of the textiles studied, the second one was detected in textiles NN 1 and 9 (Fig. 3).

Violet threads have not so far been found in the 16-17th century Persian textiles. Threads of this colour were found in Italian textile N 19 (the dyestuffs: orcein + indigo) and in the 18th century Persian velvet (the dyestuff: hematein) (Fig. 3).

The correlation tables, in Fig. 4, show some combination regularities of different dyestuffs.

The composition of mordant cations. In threads dyed by mordant dyestuffs we found the most common cations: Al^{3+} , Ca^{2+} , Mg^{2+} in red, yellow and green ones, in addition to them also cations Fe^{2+} in black and flesh-coloured ones. Mordant cations Sn^{2+} , whose use is indicated in European recipes of dyeing (2, 3), were not found in the 16-17th century Oriental textiles that were studied.

Reliable differences in the composition of mordant cations between the Turkish and Persian textiles were not found.

The results obtained demonstrate, firstly, the stability of Oriental traditions in the 14-17th centuries, and, secondly, a high technological skill making it possible to produce magnificent dyeings by means of ordinary mordants.

Vat Dyeing Characteristics. The technology of dyeing by a vat indigo dyestuff is very complicated and goes through several stages.

1. The colourless precursor indoxyl is contained in the vegetable raw material. Indigo is to be made by a fermentative separation of the glucose molecule, dimerization and oxidation of indoxyl.

2. Indigo in a blue oxidized form is virtually insoluble and is incapable of combining with fibres. In order to dye fibres it is necessary to transform it beforehand into a colourless reduced soluble form of leucoindigo. To do so, a vat is created, in which a reducing weakly alkali medium is maintained. In the vat leucoindigo is capable of penetrating fibres and, owing to OH-groups, combine with fibres as a direct dyestuff.

3. The fibres are taken from the vat into the air where O_2 oxidizes leucoindigo back into blue indigo. In such a form indigo is virtually not combined with the fibres and stays in them only by reason of its insolubility.

Before the 20th century the vat was prepared from products of anaerobic glycolysis of different organic substances including sugar and polysaccharides. It is very difficult to create and maintain for long period reducing conditions that would give a high concentrations of leucoindigo. The following characteristics were studied experimentally in order to evaluate the technological skill of vat indigo dyeing.

Intensity of indigo dyeing. This characteristic was determined microscopically on separate filaments and also by the percentage content of indigo per 100 g. of silk. The most intensively dyed threads (almost black colour) were found in Chinese texti-

Fig. 4 Preliminary distribution of studied Persian and Turkish textiles into groups according to the combinations of dyes

Textiles are underlined: — Persian
= Turkish

Significance of textiles see on p.p. 2-3

Blue dyes				Black dyes			
			2	red is absent	8		
			16	alizarin	16		
			6	bramalein		6	
12 14			12	carminic acid	12 14		
	4a 4b	2 3 8		carthamin	4a 4b	2 3	
1			15		15		1
indigo	indigo	indigo	blue is absent	black is absent	tannic	tannic	
luteolin	luteolin	walnut			indigo	indigo	
Blue dyes				Black dyes			
			blue is absent	blue is absent	12	16	
			indigo	indigo	12	16	
			indigo + luteolin	4a 4b		6 7	
			indigo + walnut	10	12		1

Fig. 4 Preliminary distribution of studied Persian and Turkish textiles into groups according to the combinations of dyes

Textiles are underlined: — Persian
= Turkish

Significance of textiles see on p.p. 2-3

le N 17 (3.0% indigo per 100 g. of silk). Dark blue threads (0.5-1.0% indigo) can also be found in the Persian textiles. In the Turkish textiles sky-blue threads prevail (0.05-0.1% indigo).

Homogeneity of dyeing of fibres in threads. Colour non-homogeneity of filaments in one thread of blue and green colour can very often be found in the Turkish and Persian textiles*. This may have resulted from imperfect vat dyeing, or been done deliberately. In the latter case the reason might have been economic and to use most efficiently the remnants of fibres dyed by indigo, or for aesthetic reasons to give threads more complex and lively shades.

Non-homogeneous dyeing of filaments prevails in blue and green threads of the Persian textiles. In the Turkish textiles homogeneous and non-homogeneous dyed filaments in threads of this colour are found in an approximately equal number.

Homogeneity of dyeing of the bulk and surface of individual filaments. If individual indigo particles cannot be seen, and fibres seem to be homogeneously dyed in blue and green filaments at large magnifications of over 300^x, it means that the size of particles is less than 1 micron. The smaller are the sizes of pigment particles, the more intensive the dyeing becomes, with a fixed pigment content in the filament volume. Therefore, an intensive homogeneous dyeing of filaments without large particles show that dyers succeeded in maintaining the reducing vat for a long time and ensured the penetration of leuco-indigo into the filaments. If large dispersed particles of indigo prevail on the surface and in the bulk of filaments, it means that the reducing vat was unstable.

Filaments homogeneously dyed throughout their volume without large dispersed particles prevail in blue and green threads of all the textiles studied.

If the volume of filaments was homogeneously and intensively dyed through, but at the same time there are large dispersed particles present, it means that fibres were vat dyed several times.

Large dispersed indigo particles were found on the surface and in the volume of filaments respectively in 50% and 30% Persian and 35% and 45% Turkish textiles studied.

If indigo particles are present only on the surface of threads and are absent in the volume of individual filaments, it means that already spun threads were dyed. This dyeing method was found in two textiles studied.

Conclusion

1. The Turkish and Persian textiles that were studied are similar by the composition of mordant cations and by technology of dyeing by the vat indigo dyestuff.
2. The most distinct differences between the textiles of the two countries are linked to the methods of obtaining red, blue, green, black and flesh-coloured threads, as well as to the number of shades of each of these colours. Differences were found in the values of M and N/M, with further investigation being required to confirm them.

References

1. Golikov V.P. Spectrofotometric Determination of red and violet dyes in museum textiles. ICOM. - Sydney, 1987.
2. Levshin V. Full dyer. Department 3, part 2. Sanct-Petersburg, 1819.
3. Agentov M. Revelation of hidden arts, Moscow University Typografy, 1769.

* Threads of other colours can also be non-homogeneous but much rarer.

ABSTRACT

The embroidery thread of a 10th century relic pouch was examined by different scientific methods. The aim of the investigations was to establish an optimal sequence of methods for obtaining the maximum information on manufacturing technique of the metal thread using as small sample as possible. Optical microscopy, scanning electron microscopy and energy dispersive X-ray analysis were used for the morphological and material tests of the two samples of about 3 mm of common length. Data show that a gilt silver strip was wound around a silk core for making the thread. Thickness and width of the metal strip, the composition and width of the silver and gold layer and the possible ways of gilding are also given.

KEYWORDS

Scientific examination, metal thread, gilt silver, manufacturing technique.

DETERMINATION OF THE MANUFACTURING TECHNIQUE OF A 10TH CENTURY METAL THREAD

Márta Járó

National Centre of Museums

H-1087 Budapest, Könyves K. krt. 40.

Attila Tóth

Research Institute of Technical Physics of the Hungarian

Academy of Sciences

H-1047 Budapest, Fóti út 56.

Erzsébet Gondár

INNOVATEX, Textile Engineering Institute

H-1103 Budapest, Gyömrői út 86.

Introduction

The relic pouch from which our metal thread samples were taken belongs to the collection of the German National Museum, Nürnberg (Inv. No.: KG 562) (See Fig. 1.).

The small (15x13 cm) bag, sewn of silk, decorated with pearls gems, gilt silver plates and gold embroidery was probably made for the order of the bishop of Hildesheim, Bernward in Trier at the end of the 10th century. It could serve for holding a Holy Crucifix relic (1).

The aim of the investigations was to establish an optimal sequence of scientific methods for obtaining the maximum information on the manufacturing technique of the metal thread using as small of a sample as possible.

We used scientific methods which have been shown to be suitable for testing metal threads (2). Darah (3) suggests to use 5-20 mm of sample but we tried to carry out the investigations with two samples less than 5 mm of common lengths.

Morphological and material tests

We used two thread samples of lengths 2.1 mm and 1.2 mm for the tests. The steps of the investigation were as it follows:

1. Optical microscopy

The study of the samples by optical microscope gives information on the morphology of the thread.

The first documentation on the thread (description, drawings and/or colour photos) can also be prepared with the help of the optical microscope (reflected light at magnification of 50-100).

In our case the samples belong to the metal thread type where metal strip is wound around a fibrous core (See Fig. 2). The metal strip looks like slightly corroded (tarnished) gilt silver, the core is greyish white.

Following the study by optical microscopy, the shorter piece of thread was unwound and the metal strip was flattened on a piece of adhesive tape. The width of the strip was measured with a built in scale optical microscope. The width of our metal strip is about 0.20 mm.

Mounting the core of the unwound sample on a microscope slide, the core material can be identified using optical microscope (transmitted light).

In our case the fibrous core as well as the longer sample (partly unwound) were attached to adhesive tape and covered by a very thin graphite layer



Fig. 1 Relic pouch dated to the 10th century

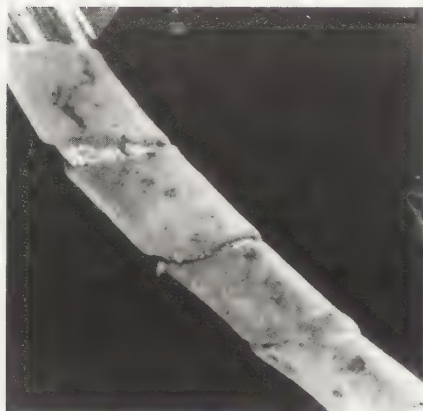


Fig. 2 The longer metal thread sample x78, scale bar= 0.1 mm

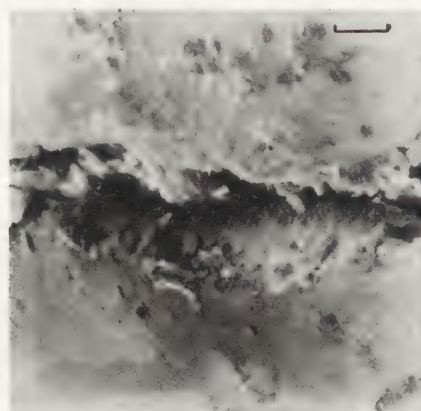


Fig. 3 SEM micrograph of the edges of the strip x1000, scale bar= 0.01 mm

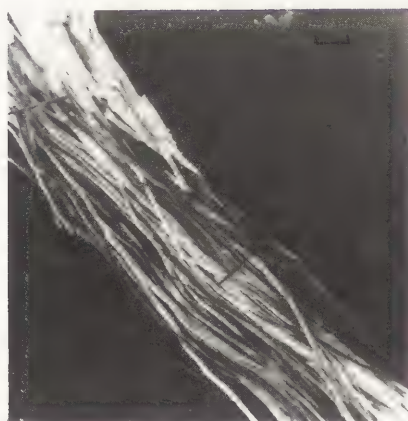


Fig. 4 SEM micrograph of the fibrous core x60, scale bar= 0.1 mm



Fig. 5 Detail of the fibrous core, typical picture of broken silk fibre x1000, scale bar= 0.01 mm

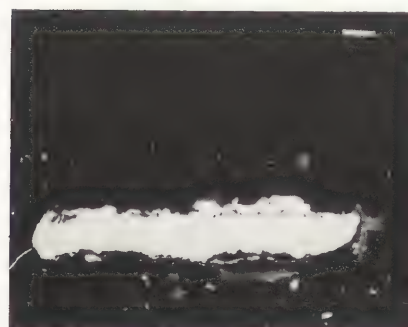


Fig. 6 SEM micrograph of the cross section of the metal strip x390, scale bar= 0.02 mm

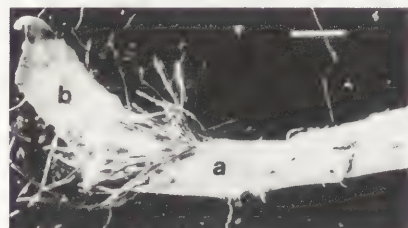


Fig. 7 SEM micrograph of a part of the longer sample, partly unwound x500, scale bar= 0.2 mm. Points *a* and *b* show the parts analysed (See Figs. 8 and 9)

(necessary for further examinations). The unwound metal strip was embedded in synthetic resin and polished for obtaining a cross section. The embedded and polished strip was also coated with graphite.

2. Scanning electron microscopy (SEM)

This method can provide further details on the manufacturing technique, the state of preservation of the metal, the corrosion products can be observed. We can identify the core material as well. The SEM micrographs taken from the examined parts complete the documentation on the metal thread. Those taken from the cross section allow the measuring of the thickness of the metal strip.

In the case of our sample, on the edges of the metal strip, the trace of a cutting tool (sharp knife or blade?) can be observed (See Fig. 3) which means that the strip was cut from a foil. The core material could be identified as silk (See Figs. 4,5). The thickness of the metal strip is about 0.025 mm (See Fig. 6).

3. Energy dispersive X-ray analysis (EDX)

Using this method the semi-quantitative analysis of the elements in the metal can be carried out. Examining the surface and back of the metal strip we can see whether our strip is made of pure metal (e.g. gold), of an alloy (e.g. silver alloyed with copper) or it is a metal covered with another one (e.g. gilt silver).

In our case the composition of the surface and back of the strip differ from each other, the strip is gilt silver (See Figs. 7-9). For a better presentation of this fact the gold and silver specific X-ray radiation was photographed (See Figs. 10,11).

The EDX method can be used for studying the cross section of the metal strip as well. It is necessary when the metal strip is made of a metal coated with another one: the element-specific pictures can show the distribution of the different sorts of metal and give information on the thickness of the different layers. The determination of the metal composition from point to point along a line on the cross section gives data to the representation of the element composition profiles. These profiles can help with discovering which kind of metal coating method (e.g. plating by heating, soldering, etc.) was

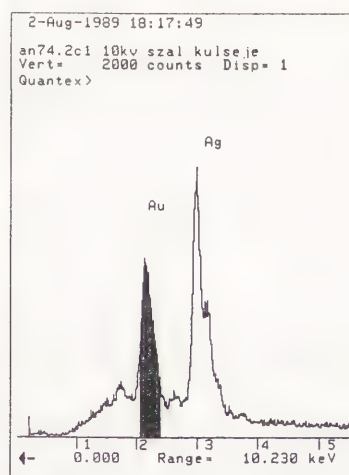


Fig. 8 Composition of the surface of the strip (point *a* on Fig. 7)

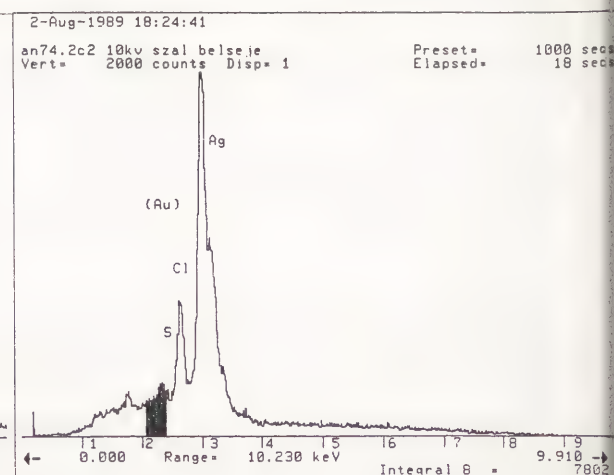


Fig. 9 Composition of the back of the strip (point *b* on Fig. 7)

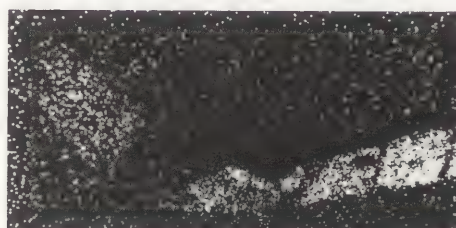


Fig. 10 Gold specific picture of the metal thread part shown on Fig. 7. Gold can only be detected on the surface of the strip.

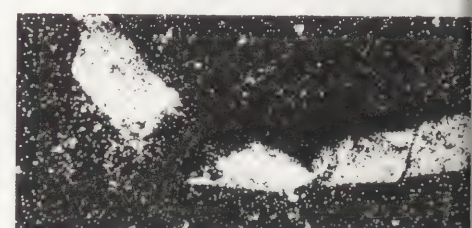


Fig. 11 Silver specific picture of the metal thread part shown on Fig. 7. Silver can be detected both on the surface and on the back of the strip, because we get information from a layer which is thicker than the gold layer on the silver strip.



Fig. 12 Detail of the cross section (SEM micrograph, x1500, scale bar=0.01 mm)



Fig. 13 Gold specific picture of the cross section part represented on Fig. 12.

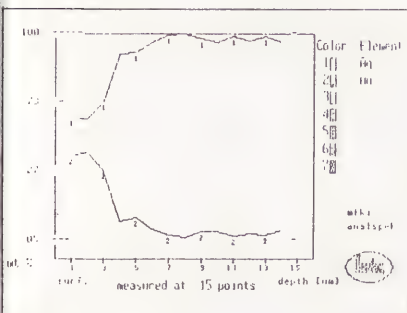


Fig. 14 Silver and gold concentration profile of the strip

used. The analysis of the metal composition gives more precise results on the cross section than on the surface or back of the strip (e.g. corrosion products, dirt particles can modify the data.)

In our case the thickness of the gold layer is about 0.003-0.005 mm (See Figs. 12,13). Examining the silver and gold concentration profile of the cross section (See Fig. 14) we can suppose that either a plating of silver with gold by heating the two metals (welding) (4) or an amalgamation process (5) was carried out. The gold-to-silver ratio on the surface (Au: cca. 30%, Ag: cca. 70%) can be explained by the forming of an alloy from the gold leaf or amalgam and the silver during heating. (With the EDX method we couldn't identify any mercury in the metal.) The silver was hammered to thin foil after gilding (both of the mentioned gilding methods needs a thicker sheet of silver because of heating). The silver contains less than 1% copper, about 0.6%.

4. Trace element analysis: atomic emission spectroscopy (AES), laser microspectral analysis (LMA)

Both methods are suitable for trace element analysis. The results can help, for instance, to decide whether fire gilding (with gold amalgam) was carried out (detection of traces of mercury). Samples prepared for SEM or EDX analysis can be used for AES or LMA methods. The graphite layer doesn't disturb the examination. Both of the methods are destructive, that means, the sample is destroyed during examination. So they can always be carried out as the last step of the investigation.

Conclusion

The morphological and material tests carried out on two metal thread samples (the common length of which was 3.3 mm) gave the following results concerning the manufacturing technique of the thread:

The metal thread was made by winding gilt silver strip of about 0.20 mm of width and 0.025 mm of thickness around a white silk core. The strip was cut from a gilt silver foil. The silver foil was certainly prepared either from a thicker piece of silver (containing about 0.6% copper) covered with gold leaf (the two sorts of metal were welded together by heating them) or piece of silver covered with gold amalgam (and heated for driving away the mercury). The gilt silver was hammered to a thin foil. The thickness of the gilding is about 0.003-0.005 mm, the gold layer is in fact a gold-silver alloy.

To our best knowledge, except for the threads coming from the excavation of Traismauer, Austria (6) no gilt silver thread has been identified as yet on textiles dated before the beginning of the 2nd millenia A.D.

Aknowledgements

The author is grateful to Ms Annelise Streiter and Ms Erika Weiland, textile restorers, German National Museum, Nürnberg, for help in the work and to Ms Dr. Leonie von Wilckens, art historian, Munich, for supervising the paper.

References

1. L. von Wilckens: "Der Reliquienbeutel des Bishops Eduard Jakob von Hildesheim", in: *Anzeiger des Germanischen Nationalmuseums*, Nürnberg, 1986): 19-25.
2. For example: E. Hoke, I. Petraschek-Heim: Microprobe Analysis of Gilded Silver Threads from Mediaeval Textiles, *Studies in Conservation* 22, (1977); L.P. Stodulski, D. Nauman, M. Kennedy: "Technical appendix: analysis of precious metal threads", in: *Fabrics in Celebration from the Collection by P. Stolz Gilfroy*, Catalog (Indianapolis Museum of Art, 1983); M. Járó: "The technological and analytical examination of metal threads on old textiles", in: *Contributions to the 4th International Restorer Seminar Veszprém*, 1983, Budapest 1984; N. Indictor, R.J. Koestler, The Identification and Characterization of Metal Wrappings in Historic Textiles Using Microscopy and Energy Dispersive X-Ray Spectrometry: Problems Associated with Identification and Characterization, *Scanning Electron Microscopy*, (II/1986); J. Darah: "Metal Threads and Filaments", in: *Recent Advances in the Conservation and Analysis of Artifacts*, (Sommer School Press, London, 1987)
3. J. Darah: op. cit. (See Ref. 2): 212.
4. W. Theobald: Technik des Kunsthandwerkes im 10. Jahrhundert, *Glaser Annales f. Gew. u. Bauw.*, 36, (1912): 369.
5. E. Hoke, I. Petraschek-Heim: op. cit. (See Ref. 2) 56.
6. I. Petraschek-Heim: Textilkundliche Untersuchungen von Stickereien aus Grab 1 in der Stadtpfarrkirche von Traismauer, *Fundberichte aus Österreich*, 16 (1977, Wien, 1978): 272.

ABSTRACT

In this first part of a continuing project, the tear strength and degree of polymerization of plain-woven cotton fabric exposed to the light of a Xenon arc lamp, with and without filters, at temperatures from 32 to 56 C and relative humidities between 30 and 75% were measured. Pseudo-first-order reaction rate constants and activation energies derived from these measurements indicate that the mechanisms of photodegradation are quite different from those encountered in heat aging.

The mechanisms of photodegradation, the role of moisture and the significance of this study for the practice of textile conservation are considered.

KEYWORDS

CELLULOSIC TEXTILES, LIGHT, AGING, HUMIDITY, COTTON, PHOTODEGRADATION, TEMPERATURE

PHOTODEGRADATION OF CELLULOSICS, PART 1: Effects of Temperature and Humidity on Tear Strength Retention

Kyung Sook Jeon and Ira Block*

Department of Textiles and Consumer Economics
University of Maryland
College Park, MD 20742
USA

Introduction

At a given temperature, the absorption of light by cellulosic materials can produce a variety of different chemical reactions. The specific chemistry is dependent upon the energy of the light absorbed, the purity of the material, and the presence of moisture and oxygen. "Direct Photolysis", the breaking of chemical bonds, occurs when ultraviolet (UV) light at wavelengths less than 340 nm is absorbed. This process is not of major importance in the museum environment, where materials are protected by glass or UV filters.

"Photosensitized Degradation" occurs when impurities, eg, dyestuffs, metal ions, degradation products, etc., in the material absorb near UV light at wavelengths between 340 and 400 nm and transfer some of this absorbed energy to a cellulose molecule (1). Light of this energy cannot cause chemical bonds to break, but can raise impurities in the cellulose to an "excited state". These excited species can then induce the cellulose molecules to react with oxygen or other reactive species in the environment. Since light of this energy range is transmitted through normal glass, photosensitized degradation is, by far, the most important photochemical reaction occurring in the museum environment and may, under some circumstances, be the dominant mode of the aging of textile objects.

In order to develop appropriate strategies and techniques for the conservation of cellulosic materials exposed to light, it is necessary to understand the mechanisms of degradation and the effects, if any, of temperature and relative humidity. In this report, the first in a series, the authors review the literature on the photochemical deterioration of cellulosic materials, and discuss the effects of changes in temperature and humidity on the tear strength and degree of polymerization of cotton fabric.

Oxygen

It has been shown (2) that oxygen is an essential element in the photochemical degradation of cellulose exposed to near UV light. Detailed studies have shown that fabrics and films aged in oxygen exhibit increased absorption in the near UV region, while those not exposed to oxygen do not (3-5). Thus, the presence of oxygen not only causes chemical modification, it enhances the capacity of light to induce oxidation.

The mechanisms of photooxidation are not well known, but it is recognized that the formation of free radicals is the first step (5). Carbonyl ($>C=O$) and carboxyl ($-COOH$) species are then created, with carbonyl being predominant (6, 7), and chain scission occurs (3). The processes leading to chain scission, and the role of the $>C=O$ and $-COOH$ species are still in doubt. It has been postulated, however, by Daruwalla (8) that the formation and subsequent reactions of hydrogen peroxide would be important, and Hon (9) has discussed pathways by which carbonyl and carboxyl species might be formed.

More recently, Lee, et al (10) have reported on the effects of commercial fluorescent lamps on high-cellulose papers. They noted that oxidation took place even when UV filters were used to protect the paper samples. They also found that exposure to light made the papers more sensitive to thermal aging. DeSimone and Block showed, in their work on Cellophane films (11), that oxidation products were $>C=O$ species and that removal of these species by reduction with sodium borohydride improved the resistance to thermal aging of the films.

In the light of the above findings, it is reasonable to conclude that the formation of carbonyl species on the cellulose chains may be the major consequence of irradiation by near-UV light, and that these products lead to further changes, such as decreases in molecular weight and increased acidity.

Moisture

The effect of moisture on photooxidation has been studied, but the results are, as yet, inconclusive. Daruwalla, et al (8) found that increased moisture, up to about 7% moisture content, led to decreases in damage, but beyond that value chemical damage increased. Hon (12) supported this finding by his measurement of free radicals; showing that the concentration of free radicals in cotton exposed to UV light decreased over the moisture content range of 5 - 7%. These results would lead to the conclusion that a relative humidity of about 55% at 20 C would be optimum for protecting against the effects of light.

Hackney and Hedley (13), however, observed no significant difference between yarns exposed, at room temperature, to sunlight at 35 - 40% RH and those exposed at 60 - 65% RH, while Hon et al (14), working with wood pulp, found that free radical concentrations increased for moisture contents up to 6.3%. Their results would lead one to argue for lower relative humidities for the display of cellulosic materials.

Temperature

The effect of temperature on photooxidation has not been well studied, although it has been recognized that the influence of this parameter is very complex (15). First, the reaction rate should change as a function of temperature; with an overall activation energy following the well-known Arrhenius relationship. However, the activation energy for photooxidation of cellulose has not been reported, so that predictions cannot be made. In addition, the moisture content of cellulosic materials changes when the temperature is altered. Consequently, an increase in temperature, which raises the chemical reaction rates, decreases the moisture content, which may also change the reaction rates. We cannot at this time, therefore, predict whether the degradation rate will rise or fall.

Reaction Kinetics

The theoretical basis for the presentation of the data is a kinetic model in which it is assumed that (1) chain scission is a first-order process, i.e., the probability of breaking a link in a polymer chain is proportional to the number of links in the chain, (2) scission is random along the chain and (3) the concentration of chromophores (light-absorbing species) is constant.

A statistical analysis (17), independent of reaction mechanism, reveals that for a small degree of conversion the degree of polymerization (DP) should follow Equation (1)

$$1/DP - 1/DP_0 = k * t \quad (1)$$

where DP_0 is the initial degree of polymerization, k is the first-order rate constant and t is the reaction time. Recently, Lee, et al (10) have shown that the model satisfactorily explains the effects of visible and near UV light on paper. It has also been shown, (18) that fabric tear strength can be substituted for DP, thereby, reducing the time and expense required. Therefore, one should find that

$$1/(\% \text{ Strength Retained}) = k * t \quad (2)$$

It should be noted that, because of the complexity of the chemical mechanisms, the k values determined in this work are pseudo first-order rate constants that describe the overall reaction.

Experimental Procedures

The fabric used in this study was Testfabrics style 400 cotton print cloth. The fabric was washed and dried twice as per AATCC Test Method No. 124, rinsed in deionized water and air dried before use.

An Atlas Electric Products Mod. 25 Weatherometer equipped with a xenon arc lamp provides the emission spectrum closest to natural sunlight, Fig. 1 (16), and was used for this study. The lamp was fitted with a soda-lime outer filter and a borosilicate inner filter to simulate sunlight behind glass.

Standard Xenon Reference Fabric for calibrating the Weather-

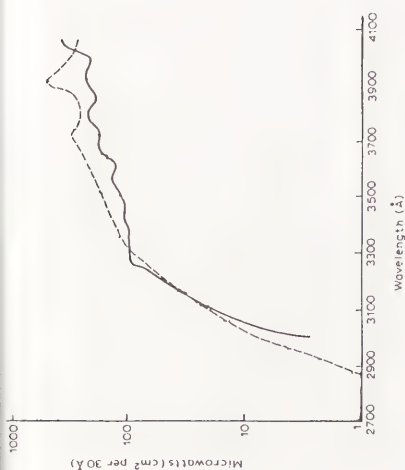


Figure 1. Emission Spectra of --- Xenon Arc Lamp and — Sunlight. (Adapted from Ref. 16)

ometer was supplied by the American Association of Textile Chemists and Colorists. This method of monitoring the lamp output provides an integrated energy output over a set time period, but does not monitor power fluctuations.

Tear strength was measured by the Elmendorf falling pendulum method according to ASTM D1424.

Results and Discussion

Typical results, appropriate to this paper, are shown in Figs. 2 - 6 and Tables I and II. Figure 2 shows a plot of the inverse of percent strength retained ($1/(\% \text{ SR})$) vs time for cellulose exposed to a Xenon arc lamp at 40 C and relative humidities of 30, 50 and 75%. The lines are plots of the linear regression equations. It is apparent that the data fit the model.

In Fig. 3, typical effects at constant humidity are shown. Here are seen the results for different temperatures at RH = 50%. The lines are plots of the regression equations, and again show that the kinetic model is valid.

Table I, a summary of the results of this portion of the study, lists the reaction rates for the degradation of cotton cloth at different temperatures and humidities. The numbers in parentheses are the regression coefficients found for the linear regression of the data fitted to the kinetic model of Equation 1.

TABLE I

Pseudo First Order Rate Constants at Different Temperatures and Relative Humidities

Temperature (C)	Relative Humidity (%)		
	30	50	75
32	-	0.79	1.17
40	0.87	1.37	1.94
50	1.63	2.14	3.20
56	2.39	3.15	-

Figure 4 depicts the data in Table I. Here, the reaction rates are shown as a function of relative humidity for each temperature. It is clear that (1) the rate increases with increasing temperature for each relative humidity and (2) the rate at each temperature increases with rising relative humidity. It is also of interest to note that the slopes of the lines increase with increasing temperature. That is, at the lower temperatures moisture is less important than at the higher temperatures. These findings are in apparent contradiction to the predictions of Daruwalla (8) and Hon (12), but seem to support the studies by Hackney and Hedley (13) and Hon et al (14).

A more detailed analysis is shown in Fig. 5, where the slopes of the lines in Fig. 4 are plotted as a function of temperature. The line passing through the three lower points is the regression line ($R^2 = 0.992$). It may be seen that as the temperature decreases the slope approaches zero. Thus, it would be expected that at ambient temperatures, about 20 C, changes in humidity would have no discernible effect. Since the influence of moisture is less at lower temperatures than at high, these results may also explain why Hackney and Hedley (13) did not find relative humidity to be an important factor in their investigation.

It is not clear if the datum point at 56 C indicates a roll-off in the effect of moisture. Further work is needed to clarify the humidity effects at higher temperatures.

Because the data of Table I can be so well fitted to the kinetic model of Equation 2 ($R^2 > 0.9$), it may be assumed that the aggregate chemistry leading to the loss in tear strength can be modeled as a pseudo first-order chemical reaction. Then, from the rates obtained from the $1/(\% \text{ SR})$ vs time plots, it is possible to determine the reaction rates at different

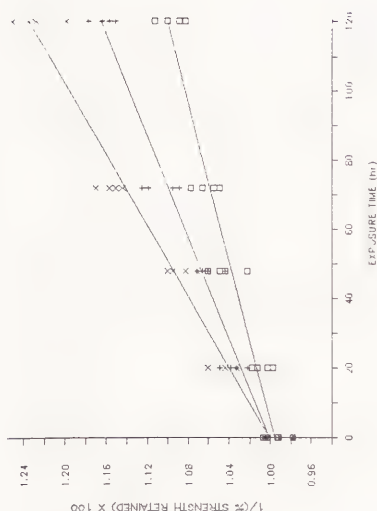


Figure 2. $1/(\% \text{ Strength Retained})$ vs Exposure Time for Cotton Fabric Irradiated with a Xenon Arc Lamp at 40 C: \square = 30, $+$ = 50 and \times = 75 % RH.

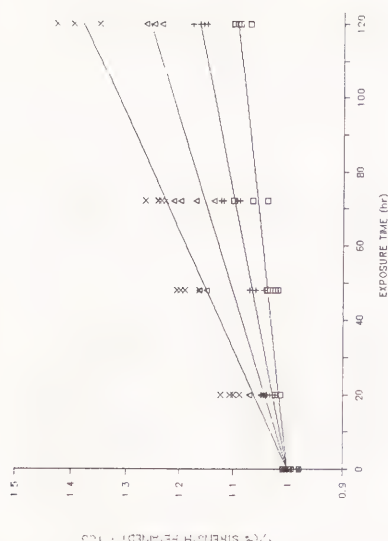


Figure 3. $1/(\% \text{ Strength Retained})$ vs Exposure Time for Cotton Fabric Irradiated with a Xenon Arc Lamp at 50% RH at \square = 32, $+$ = 40, Δ = 50 and \times = 56 C.

temperatures for each relative humidity.

As shown in Fig. 6, these reaction rates can be fitted to the Arrhenius Equation

$$\ln(K_{\text{hot}}/K_{\text{cold}}) = E_a/R * (1/T_{\text{cold}} - 1/T_{\text{hot}}) \quad (3)$$

where K = pseudo first-order reaction rate constant and T = absolute temperature, for the purpose of determining the overall activation energy, E_a , at each relative humidity.

The overall activation energies as a function of RH are listed in Table II. At the 0.05 confidence level, there are no statistically significant differences among the values, so that E_a is found to be approximately 11.5 ± 1.5 kcal/mole. This value is substantially different from that for the thermal aging of cellulose, about 26 kcal/mole (19), and indicates that the reaction mechanisms for the photochemical aging of cellulose are significantly different from those of thermal aging.

TABLE II

Overall Activation Energies at Different Relative Humidities

Relative Humidity (%)	Activation Energy (kcal/mole)
30	12.8
50	11.0
75	10.9

The low value of E_a means that the photochemical reaction rates have a relatively low sensitivity to changes in temperature. For example, the rate of photochemical degradation at 20 is about 10% that at 56 C. By contrast, the rate of thermal degradation at 20 C is only about 1% that at 56 C.

Conclusions

It is shown that, over the range studied, the rate of light-induced degradation of cotton cloth increases monotonically with both temperature and humidity with pseudo first order rate constants ranging from a low of 0.79 at 32 C and 50% RH to a high of 3.2×10^{-5} /hr at 50 C and 75% RH. A protective effect of moisture was not found.

Moisture is more important at the higher temperatures than at the lower temperatures, with the effect of changes in relative humidity approaching zero at room temperature.

The overall activation energy for the light-induced degradation of cotton cloth is only about 11 kcal/mole, much less than that for thermal aging, so that the photochemical reaction rates have a relatively low sensitivity to changes in temperature.

References

1. Robinson, H M and Reeves, W A, "A Survey of the Effect of Light on Cotton and Other Cellulosic Fabrics", American Dyestuff Reporter, 50 (1961): 17-31.
2. Launer, H F and Wilson, W K, "The Photochemistry of Cellulose, Effects of Water Vapor and Oxygen on the Far and Near Ultraviolet Regions", Journal of the American Chemical Society, 71 (1949): 958-962.
3. Hon, D N S, "Photooxidative Degradation of Cellulose: Reactions of the Cellulose Free Radicals with Oxygen", Journal of Polymer Science, 17 (1979): 441-454.
4. Daruwalla, E H and Narsian, M G, "Detection and Identification of Acid-Sensitive Linkages in Cellulose Fiber Substrates", TAPPI 49 (1966): 106-111.
5. Desai, R L and Shields, J A, "Photochemical Degradation of Cellulose Material", Die Makromolekulare Chemie 122 (1969): 134-144.

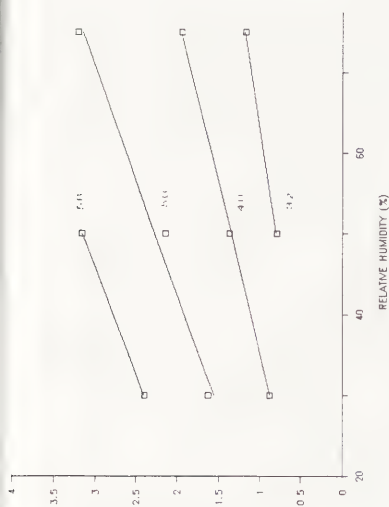


Figure 4. Pseudo First Order Reaction Rates vs Relative Humidity for Cotton Fabric Irradiated with a Xenon Arc Lamp at Different Temperatures.

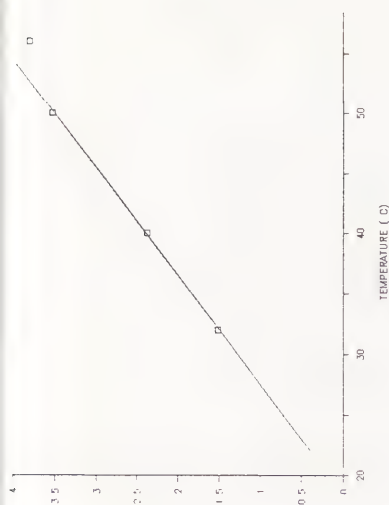


Figure 5. Humidity Response (Slopes of Fig. 4) as a Function of Temperature for Cotton Fabric Irradiated with a Xenon Arc Lamp.

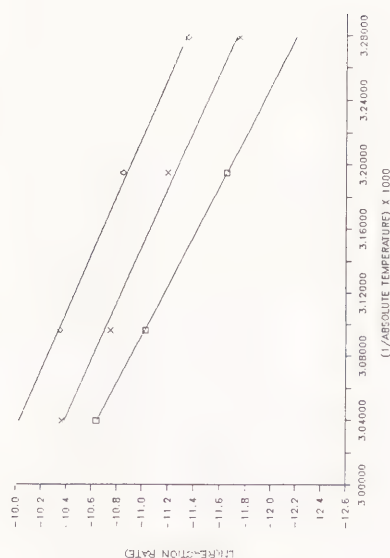


Figure 6. Arrhenius Plots for the Loss of Tear Strength for Cotton Fabric Irradiated with a Xenon Arc Lamp at \blacksquare = 30, \times = 50, and \blacklozenge = 75 % RH.

6. Reine, A H and Arthur, J C, Jr, "Photochemistry of Cotton Cellulose: The Direct Action of Near Ultraviolet Light on Purified Fibrous Cotton Cellulose", Textile Research Journal, **40** (1970): 90-92.
7. Desai, R L, "Photodegradation of Cellulosic Materials - A Review of the Literature", Pulp and Paper Magazine of Canada **69** (1968): 53-61.
8. Daruwalla, E H, D'Silva, A P and Mehta, A C, "Photochemistry of Cotton, Part 1: Behavior During Exposure to Carbon-Arc and Solar Radiations", Textile Research Journal **37** (1967): 147-160.
9. Hon, D N S, "Formation of Free Radicals in Photoirradiated Cellulose and Related Compounds". Journal of Polymer Science **14** (1976): 2513-2525.
10. Lee, S B, Bogaard, J and Feller, R L, "Damaging Effects of Visible and Near-Ultraviolet Radiation on Paper", in Historic Textile and Paper Materials II: Conservation and Characterization, ACS Symposium Series 410, Zeronian, S H and Needles, H L, Eds. American Chemical Society, Washington, DC, (1989): 54-62.
11. DeSimone, L and Block, I, "Ultraviolet and Infrared Analyses of Artificially Aged Cellophane Film", in Historic Textile and Paper Materials II: Conservation and Characterization, ACS Symposium Series 410, Zeronian, S H and Needles, H L, Eds. American Chemical Society, Washington, DC, (1989): 220-238.
12. Hon, D N S, "Formation of Free Radicals in Photoirradiated Cellulose, II: Effect of Moisture", Journal of Polymer Science **13** (1975): 1347-1361.
13. Hackney, S and Hedley, G, "Linen Canvas Artificially Aged", Preprints of the 7th Triennial Meeting, Copenhagen, the ICOM Committee for Conservation, Paris, (1984): 84.2.16-84.2.21.
14. Hon, D N S, Ifju, G and Feist, W C, "Characteristics of Free Radicals in Wood", Wood and Fiber, **12** (1980): 121-130.
15. Graminski, E L, Parks, E J and Toth, E E, "The Effects of Temperature and Moisture on the Accelerated Aging of Paper", in Durability of Macromolecular Materials, Eby, R K, Ed., ACS Symposium Series 95, American Chemical Society, Washington, DC, (1979): 341-355.
16. Atlas Electric Devices Company, "Fade-o-meter and Weatherometer Manual", (1988)
17. Jellinek, H H G, in Aspects of Degradation and Stabilization of Polymers, Elsevier, New York, (1978): 2.
18. Block, I and Roy, A M, "Treatment of Cellulosic Textiles with Sodium Borohydride", Preprints of the 8th Triennial Meeting, Sydney, the ICOM Committee for Conservation, Paris, (1987): 345-351.
19. Block, I and Kim, H K, "Accelerated Aging of Cellulosic Textiles at Different Temperatures", in Historic Textile and Paper Materials, Conservation and Characterization, Advances in Chemistry Series 212, Zeronian, S H and Needles, H L, Eds. American Chemical Society, Washington, DC, (1986): 411-426.

Acknowledgements

The authors wish to thank Ms. Laura DeSimone for her help with laboratory procedures and the General Research Board of the University of Maryland for its financial aid.

ABSTRACT

This paper outlines current premises for adhesive textile conservation treatments. It covers three main themes: firstly, adhesive treatments are only suitable for deteriorated painted textiles and powdery degraded silks from the turn of this century; secondly, adhesives should not penetrate textiles and therefore must be applied as sparingly as possible; and finally, emanating from a long-term Canadian Conservation Institute adhesive testing program, certain textile adhesives are tentatively discussed.

KEYWORDS

CONSERVATION; TEXTILE;
TREATMENT; ADHESIVE;
APPLICATION; BACKING FABRIC

THE USE OF ADHESIVES IN TEXTILE CONSERVATION

Michaela Keyserlingk
Canadian Conservation Institute
Department of Communications
1030 Innes Road
Ottawa, Ontario, K1A 0C8, Canada

Introduction

The aim of this paper is to outline some current premises for adhesive textile conservation treatments. To this end, three themes will be discussed: when to use an adhesive treatment, what can be expected from application methods, and how to choose an appropriate adhesive.

The textile conservation field has been traditionally divided into those who use adhesives and those who do not. For over a century these two groups have argued the pros and cons of their beliefs.¹ Many conservators seem to have aligned themselves behind one of the two groups. Most have done so, at least in part, out of loyalty to their teachers, often leaders in their fields.² However, more often, textile conservators have simply lacked the opportunity to study and experiment with unfamiliar conservation methods.

Scientific and practical textile conservation knowledge about sewing and adhesive methods has made great advances since the Second World War.³ Therefore, the question should no longer be "to glue or not to glue", but when to glue and especially what application methods to employ. The use of adhesives is not a tool for the dilettante who cannot sew, but neither should the sewer condemn out of hand the use of adhesives.

For the purpose of this paper, methods such as embedding textiles between plastics,⁴ or sewing through textiles with paint layers will not be discussed because everybody agrees that such earlier treatment procedures are professionally unacceptable. It is true that a few conservators will still execute adhesive treatments badly or use unstable adhesives. Others employ stitching methods of questionable quality. The argument that the latter is easier to reverse than the former is not always correct. Sometimes an overabundance of improper stitching can leave as much permanent damage as an improper adhesive treatment.

When to Choose an Adhesive Treatment

For many years textile conservators at the Canadian Conservation Institute believed that they would never use adhesive treatments. It took some time to realize that some serious conservation problems were being ignored. The treatment challenge came in the form of painted banners where an oil medium had been used, and Victorian embroideries where embroidery stitching was combined with drawings in either ink or gouache. The question arose of how best to secure tears and losses in the painted areas. It had been shown that pressure mounts were not a satisfactory answer. Paint layers should not come in direct contact with glass or plexiglass as glass pressure may flatten a paint layer and cause it to stick to the glass.⁵ A possible route was to investigate the use of an adhesive.⁶

A second challenge arose from our attempts to conserve textiles produced after the second industrial revolution. Most European conservation laboratories do not deal with artifacts manufactured after 1860 since they are fully occupied with conserving their large collection of older textiles. However, many North American textile collections, especially those belonging to smaller and medium sized museums, hold an abundance of more recent clothing and household items. Since the 1860's, fabrics have been subjected to chemical treatments⁷ such as weighting, bleaching, colouring with unstable synthetic dyes, and coating. Over time, these treatments resulted in serious fibre degradation.⁸ Many of these textiles are now very deteriorated and powdery to the touch. Silks have often become so fragile that they will fracture if pierced by a needle. As a last resort, CCI textile conservators began to experiment with adhesive treatments to hold these fragments together.

If pressed for a general rule about when to use an adhesive treatment, the above two categories - painted textiles and degraded 19th century textiles - could be typical candidates for adhesive treatments. In our experience, we have not encountered

the need for adhesive backings for unpainted textiles predating 1860. Obviously there are exceptions which must be left to the discretion of the professional.

Application Methods

Most textile conservators learned their first couching stitches from conservators who, through many years of experience, knew how best to apply them, when to use them, and how to space them. On the other hand, some conservators seem to believe that adhesive treatments can be learned without practice but simply read and copied from the literature. Case histories are certainly helpful to learn about which adhesives were used, in what concentration and for what kind of a treatment. But the actual application method has to be learned by experience just as one acquires good couching skills. Conservators who do not use adhesives are sometimes faced with an artifact, as for example a painted dress from the 18th century, that suggests the use of an adhesive.⁹ Since they try to avoid being condemned as "gluers," they refuse to solicit help from someone knowledgeable in the application of adhesives, and so tend to muddle ahead on their own. Techniques cannot be learned from the literature alone.

Like conservators who have accumulated years of sewing experience, many textile conservators who use adhesives have spent years perfecting their methods. They have with time developed various application methods for different adhesives, which can be changed and adapted to different needs. Some current principles regarding application follow.

Adhesives which are used for textile treatments have to stay reversible over many years. They have to be chemically stable, should not cross-link on aging, and should not penetrate an historic textile. The bond should be as weak as possible, while at the same time strong enough to secure and support the deteriorated textile. Because the best bonding occurs when surfaces are clean, wet or chemical cleaning should precede an adhesive treatment. When an historic textile is to be treated by applying a backing held in place by an adhesive, all warp and weft threads should be perfectly aligned. If the adhesive bond is activated by heat, temperatures employed should not further deteriorate fibres or harm paint layers. Where loss areas in the textile expose the adhesive-coated backing fabric, the exposed adhesive should be removed to avoid adhesion of dust and the possibility of textile surfaces sticking to each other.

Unlike a consolidant, an adhesive should not be applied directly to a textile. Instead, the diluted adhesive is sprayed onto a stretched backing fabric or lightly brushed onto a fabric laid out on a release surface such as teflon coated fibreglas. The aim is to use as little adhesive as possible to obtain a nap bond only. Backing fabric made of a loose, fine weave require less adhesive for an effective nap bond than compact, densely woven materials.¹⁰

The support or backing fabric which most conservators use for adhesive treatments is either Stabiltex, a polyester fabric, or silk crepeline. These two materials have fine, plain weave structures and are almost transparent. Silk crepeline can be dyed by the conservator to any required shade. Stabiltex is usually dyed by the manufacturer, since the dyeing process requires chemicals which pose greater health hazards than those needed for dyeing protein fibres and also require high temperatures which are difficult to produce in most conservation laboratories. Stabiltex offers greater resistance to aging and is stronger than silk crepeline. It is more opaque, is more difficult to handle because it can be quite electrostatic, and does not conform to unevenness in historic textiles. This can result in problems with some textiles such as painted flags if the unpainted silk is distorted from the weight and stress caused by the painted areas. When the flat, adhesive-coated Stabiltex is heat-set to uneven areas in the textile, these areas have the tendency to lift off in blisters from the Stabiltex and to return to their original shape.

Silk crepeline can be sufficiently deformed to fit a certain amount of unevenness in the textile to be backed. On the other hand, it deteriorates faster especially when exposed to light, but this process can be retarded. When crepeline is used as a backing, its exposure to light is necessarily minimal. The author believes that silk crepeline coated with an adhesive such as an acrylic might last longer than uncoated silk fibers.

Good conservation techniques are as easy to detect in an adhesive as in a stitching treatment, although it is admittedly more difficult to judge an adhesive's longterm behaviour. In order to evaluate an adhesive's stability, close cooperation with conservation scientists is essential.

Types of Textile Adhesives

Different stitching methods are employed to attach a textile to its backing. For example, depending on the kind of damage either a couching or whip stitch is used to secure an area of loss. There are also similar alternatives when an adhesive treatment is chosen. The decision about which adhesive and application method might be correct is dictated in part by the condition of the artifact and its original construction. Oil-painted silk banners will need more adhesion because of the paint layer's additional weight than a lighter stable embroidery on powdering and splitting silk. Also, the adhesive bond will have to be stronger to support a three dimensional textile such as a costume.

Many adhesives on the market either bind textile layers to each other or reinforce weave structures. They differ both in chemical form and physical properties. Only a few of them are presently employed in textile conservation.¹¹

Textile conservators generally use adhesives which can be divided into five main chemical groups: starches, polyvinyl acetates, polyvinyl alcohols, acrylic resins, and ethylene - vinylacetates. Adhesives should be chosen which will not change even after many years of aging. They should have a neutral pH, not produce dangerous degrading volatiles, not yellow or shrink, and should maintain their cohesive strength and flexibility. Which adhesives best possess these qualities?

To help answer these questions, the Canadian Conservation Institute started an Adhesive Testing Program in 1983 under the responsibility of conservation scientist Jane Down.¹² Two adhesive groups were chosen for the first round of testing, polyvinylacetates (PVAC) and acrylic resins. To keep the number of adhesives to be tested to a manageable size, a screening procedure was established. First a comprehensive list was drawn up of PVAC and acrylic resins already used in conservation together with commercial products showing conservation potential.

Following chemical analysis, they were grouped according to their chemical types. As a result, 27 PVAC's and 26 acrylic products were selected to undergo full testing procedures. The chosen adhesives are still being aged naturally at room temperature in two groups, one in the dark and the other under lights. The two adhesive groups are re-tested on a yearly basis for pH, emission of harmful volatiles, yellowing, strength, flexibility, shrinkage, softening point, glass transition temperature and removability.

From this group of adhesives tested, six are employed for textile adhesive treatments: Mowilith DMC2 and Mowilith DM5 produced by Farbwerke Hoechst; Vinnapas Dispersion EP1 manufactured by Wacker Chemicals Ltd; Beva 371 distributed in North America by Tallas; Acryloid F 10, a product of Rhom and Haas; and Lascaux 360HV manufactured by Alois K. Diethelm. The first four adhesives are vinylacetate copolymer products, while the last two are acrylic products. These six adhesives are currently being evaluated in the Adhesive Testing Program.

Interim results are published as they become available.¹³ Although caution must be used in interpreting these preliminary results, some trends have been observed which are relevant for selecting textile conservation adhesives. Since these are commercial products, the manufacturers may vary their formulas over time. Such changes would influence not only their desirable handling properties but also their inherent stability.

Poor results achieved with an unsuitable adhesive can certainly influence a conservator's opinion about the use of adhesives on textiles in general. In many cases, an informed judgement has to be made. Certain adhesives may have superior handling properties, while their stability may be slightly less. One could either replace the adhesive with another more stable product, or proceed with the awareness that the longterm stability of the artifact is the most important consideration. To reach the right decision, it is important to know both the chemical behavior and the handling properties of adhesives.

Mowilith DMC2 is an emulsion which has been used in textile conservation since the late 1950s. Generally this adhesive is 25% diluted with distilled water, then brushed onto Stabiltex laid out on Teflon-coated fiberglass. Starting from the center out, the backing fabric is coated thoroughly with the adhesive, and then left to dry. The adhesive-coated backing fabric is then heat-set at 60°C to the back of the prepared textile. Depending on treatment needs, there are various other application methods for this adhesive.¹⁴ Most conservators using Mowilith DMC2 do not remove it from areas where the adhesive is exposed because of losses in the textile.

Mowilith DMC2 is currently performing well in the testing program. It has remained neutral after 2 years of aging and is not releasing excessive amounts of harmful volatiles such as acetic acid. The DMC2 samples are not yellowing and their flexibility appears to remain unaltered.

A number of conservators use Mowilith DMC2 in a mixture with Mowilith DM5 (1 part DMC2, 1 part DM5, 5/6 parts distilled water). The preparation of the adhesive-coated backing fabric is similar to that described for Mowilith DMC2. Mowilith DM5 is very tacky, giving this mixture initially a much stronger adhesive bond. Since the combination of these two adhesives turns the backing fabric more shiny and visible where exposed, conservators remove the adhesive in those areas with alcohol.¹⁵

Mowilith DM5 has not performed as well as the DMC2 in the testing program. The dried film has a pH of 4, which scientists consider too acidic for use on cellulosic and proteinaceous material. Mowilith DM5 has three more drawbacks: it is cohesively weak, it exhibits severe creep, and it is very tacky at room temperature. As might be expected, a mixture of the two adhesives performed better than Mowilith DM5 alone. But this mixture still remained tacky and some acidic volatile emissions were detected.

Vinnapas EP1 is another emulsion which can be brushed in either a 10% or 50% solution onto a backing fabric - layed out flat onto Mylar or polyethylene - until a solid film of adhesive is produced.¹⁶ It is also heat-set between 60° and 70°C. For this and all the other heat-set methods silicone release paper or teflon coated fiberglass is placed between the spatula or iron and the artifact. No references were found to indicate whether the adhesive is usually removed where visible. Because the adhesive is fairly sticky at room temperature, a textile treated with it is best stored between silicone-release paper.

Under testing, Vinnapas Dispersion EP1 has begun to exhibit a few problems. Although initially neutral, it is becoming unacceptably acidic after light aging. This is also reflected in an increase in volatile emissions upon light aging. It has not yellowed or lost its flexibility, but it remains tacky at room temperature.

Lascaux Acrylic Resin 360 HV is the third of the emulsion adhesives discussed here. However, it is hardly ever used for adhesive textile backing, but often as a paint consolidant or when display fabrics have to be glued to a plastic or wood mount. Slightly diluted, it is brushed onto Stabiltex which is employed as a temporary facing for paint layers. Very low temperatures or the application of pressure activate the adhesive.

Textile Conservators have reported good results after mixing soft 360HV with the firmer Lascaux 498HV in a ratio of 1:2 or 1:1 and then diluting the resin mixture with distilled water in a ratio of 1:8 or 1:10.¹⁷ Coating a backing fabric with this mixture is as described above. It is first brushed on and then heat-set between 40°-70°C.

Lascaux 360 HV performs fairly well in the program. It remains neutral and flexible and does not yellow, but it remains tacky at room temperature. Lascaux 498 HV, however, is not in the testing program, so a mixture of the two cannot be judged.

The fifth adhesive, Acryloid F 10, works well when used on flat textiles where only a very light nap bond is needed. Its handling properties are similar to those of another well-known adhesive, Lascaux Acrylic Resin P550-40TB, which is used for this purpose as well. Acryloid F10 is applied to the backing in a 1:8 solution with either toluene or mineral spirit. It is brushed lightly onto a backing fabric laid out on teflon-coated fiberglass. Once the solvent has evaporated, the backing is heat-set at 60°C to the back of the textile.¹⁸

In tests, Acryloid F10 has remained neutral and has not yellowed with age, but it seems to become slightly brittle with age.

The final adhesive, Beva 371, is effective where a stronger adhesive bond is required. A mixture of one part Beva to two parts toluene or three parts white spirit is sprayed onto the backing fabric.¹⁹ Unlike other adhesives, the same bond strength is not achieved when Beva is brushed on. Longer and higher temperatures are needed to activate the brushed adhesive and the bond obtained is much weaker. Conservators experienced with both Beva 371 and Acryloid F10 use mixing solvents to remove exposed adhesive from the backing once heat setting has been completed. In CCI's testing program Beva 371 has remained neutral and fairly flexible with age but it is yellowing.

What kind of conclusions can textile conservators draw from these tests? Firstly, one should keep in mind that only interim results are available and we still await the final scientific report. Secondly, other textile adhesives from chemical groups such as starch and polyvinyl alcohol, have not yet been tested. Thirdly, for the time being, it is advisable to exercise some caution about adhesives which on aging continue to have or develop a low pH. Fourthly, care should also be taken with adhesives which remain sticky at normal room temperatures, since dust will adhere to them and could stick textile surfaces to one another if not stored properly. Finally, an adhesive's toxicity also dictates its choice. If proper extraction and ventilation is not available, emulsions such as Mowilith DMC2 may turn out to be the best. But even emulsion adhesives sometimes need stronger or toxic solvents such as toluene to remove excess adhesive from exposed backing fabrics where parts are missing in the original textile. When adhesive treatments have to be reversed solvents are necessary not only for the solvent type adhesives but also for the emulsions. When only a nap bond exists between the artifact and the backing fabric, reversibility is also possible in water. When the adhesive treated textile is placed in water, the silk fibers swell and the adhesive coated backing fabric can be gently pulled away from the artifact.²⁰

Conclusion

This paper outlines some major premises for better adhesive textile conservation treatments by focusing on when to use adhesives, how to apply them, and what characteristics they possess. It hopes to stimulate exchange of information among textile conservators experienced in adhesive treatments, and to encourage conservators who have not yet worked with adhesives to consider this treatment method more seriously. In the future more textile conservators will have to reach for adhesives to treat painted or modern textiles. Further research into this treatment area is vital not only in order to clarify adhesives' chemical and physical behaviour, but also to improve application methods.

Endnotes

1. W. Erben, "Über die Behandlung alter Fahnen und Standarten," Zeitschrift für historische Waffenkunde, 3(1902/03), 214-217. See also . H. Bach, "Über die Erhaltung alter Fahnen," Ibid., 158-160.
2. M. Flury-Lemberg, Textile Conservation and Research, (Bern: Schriften der Abegg-Stiftung, 1988), 11.
3. Ibid., 14.
4. Ibid., 50.
5. M.T. Worch, E. Jaeger, "Zur Restorierung zerstörter Textilien," Restauro, vol.94, No.3 (1988): 167-172.
6. M. Keyserlingk, "Current Treatment of Painted Textiles at CCI", Preprints IIG-CG Conference (Victoria, B.C.,1987), n.p.
7. J. Chiltick, Silk Manufacturing and its Problem, (New York: James Chiltick, 1913), 30-49.
8. M. Horswill, "Research Report: Save the Silks! Protection for Weighted Silk Costumes," Dress, vol.14 (1988): 93-97.
9. L.M. Smith, "When Textiles are Paintings," in Symposium 86, The Care and Preservation of Ethnographic Materials, eds. R. Barclay et als, (Ottawa, C.C.I., 1987): 200-206.
10. W.Heiber, "Die Dublierung mit Gewerberasterhaftung," Zeitschrift für Kunsttechnologie und Konservierung, vol.2 (1987): 82-89.
11. N.S. Yates, "Results from a Questionnaire on the Conservation Treatment of Painted Flags and Banners", in ICOM Preprints 8th Triennial Meeting, vol.1 (Sydney, 1987): 427-430.
12. J.L. Down, "Adhesive Testing at the Canadian Conservation Institute, Past and Future" IIC - Conference, (Paris 1984)
13. J.L. Down, W.R. Scott, "Report on Adhesive Testing at the Canadian Conservation Institute", Symposium 88, in Proceedings of Historic and Artistic Works on Paper, (Ottawa, C.C.I., 1990): in press.
14. S. Landi, The Textile Conservator's Manual (London: Butterworth, 1985), 109-117.
15. K. van Nes, A. Kipp, "Treatment of a Gonfalon", in Symposium Conservation of Flags (Amsterdam, Rijksmuseum, 1980): 112-115.
16. F. Lennard, "The Conservation of the United Tin Workers' Society Banner of 1821", The Conservator, no. 13 (1989): n.p.
17. M.T. Worch, E.Jaeger, "Zur Restorierung zerstörter Textilien" Restauro, vol.94, no. 3 (1988): 161-172.
18. P. Maeder, "Methods of Conservation and Restoration at the Swiss National Museum", in Symposium Conservation of Flags: 117-119.18.
19. N.T. Muir, N.S. Yates, "The Treatment of Painted Flags and Banners at the National Maritime Museum, Greenwich," in ICOM Preprints 8th Triennial Meeting: 397-401.
20. C. van Nes, "Bemerkungen zur Reversibilität einer Klebstoffdublierung in der Textilienkonservierung," in Fourth International Restorer Seminar, vol.2 (Budapest, National Centre of Museums, 1984): 183-188.

ABSTRACT

This paper reports the results of the first stage of a major project currently in progress at The British Museum. The aim of the project is to evaluate the effect of aqueous, solvent and mechanical cleaning on woven textiles made of natural fibres so that the most effective and least damaging processes for textiles in various states of degradation may be identified. Modern undyed cotton, wool (Doctor's flannel), linen and silk have been immersed in tap and distilled water, standard textile washing solution, non ionic detergent and saponin. The effect of rinsing in running water was also evaluated. Treated samples were examined by eye and by optical microscopy. Measurements were made to determine changes in dimension, colour, molecular weight and strength.

The results suggest that silk and linen are less stable to aqueous washing than cotton and wool. Standard textile washing solution was the most effective washing agent for cotton, linen and wool, while saponin was more suitable for silk. Fast flowing tap water was the most damaging treatment for all samples.

KEYWORDS

CLEANING, WASHING, COTTON, WOOL, LINEN, SILK, VISCOSITY

INVESTIGATION INTO THE EFFECTS OF CLEANING NATURAL, WOVEN TEXTILES BY AQUEOUS IMMERSION

Yvonne Shashoua,
Department of Conservation,
The British Museum,
London WC1B 3DG.

1. Introduction

When textiles are to be cleaned, current practice in the Department of Conservation at The British Museum, is to examine the condition of the fibres, the type of soil present, the fastness of the dyes and the construction and size of the object. If the textile is considered suitable for aqueous cleaning, immersion in either distilled water or standard textile washing solution, sometimes with agitation, is employed.

The aim of this investigation was to evaluate the effects of aqueous cleaning treatments on the optical, chemical and physical properties of textiles and thereby establish a method of selecting the appropriate washing agent for a particular textile. The initial stage of this work was to investigate the effect of the techniques in use on modern textile substrates. In conjunction with conservation staff, modern textiles were selected for the initial study, with characteristics similar to those of materials in the collection.

Undyed cotton, wool, linen and silk were immersed in tap and distilled water, standard textile washing solution, Synperonic N (a non-ionic detergent) and saponin extract. Washing under running tap water was also evaluated. Treated samples were examined by eye and by optical microscopy. Measurements were made to determine changes in dimension, colour (using UV/visible reflectance spectroscopy), molecular weight (using viscometry) and strength (using tensile testing). The results were compared with untreated control substrates. The pH and conductivity of wash liquors were also measured.

The project followed a complete factorial experimental design. The purpose of such a design was to ensure that each treatment and textile combination were compared on an equal basis.

2. Experimental details and results**2.1 Sample Preparation**

All of the textiles contained fillers which were removed by boiling wool and silk in distilled water for 15 minutes and cotton and linen for 30 minutes. The filler in the wool, cotton and linen was identified as starch, and its removal was indicated by a negative test with iodine solution. Samples were allowed to dry on polythene sheets at room temperature for 48 hours, before being cut into 2cm x 8cm strips along the direction of the warp. High density Japanese silk was tested both with and without the filler. The filler was identified as gelatine by Fourier Transform Infrared Spectroscopy. Samples of each textile were assigned to the treatments at random, by being drawn from a bag, and replicate measurements of each technique were made in order to minimise the effects of inhomogeneity of weave.

2.2 Washing Technique

The effect of five washing techniques, immersion in tap and distilled water, standard washing solution, Synperonic N and saponin solution and a running rinse were investigated. All processes were duplicated.

2.2.1 Immersion in water

Samples were immersed in 30ml of tap and distilled water for 5, 15, 30, 60 minutes and overnight and dried on polythene sheets for 24 hours at room temperature before testing. Analysis of the tap water showed that it had a mean hardness of 296 mg dm⁻³ based on calcium carbonate and a mean total dissolved solids content of 444 mg dm⁻³, suggesting it to be very hard water (1).

2.2.2 Immersion in standard textile washing solution

Samples of each textile were immersed in a 500ml bath of 1% standard textile washing solution (0.005g of carboxymethylcellulose, 0.001g sodium triphosphosphate and 0.01g Synperonic N dissolved in 100g of distilled water), for 15 and 60 minutes (2). One set of samples was dried on polythene sheeting at room temperature, without rinsing to remove the washing solution. The other was rinsed by immersion in four, successive baths of distilled water (30ml each) for 15 minutes. The liquor from each bath was retained. After rinsing the samples were dried.

2.2.3 Immersion in Synperonic N solution

Textile samples were immersed for 15 minutes in a 500ml bath of 1% v/v of Synperonic N, prepared with freshly distilled water. Samples were either dried or rinsed prior to drying as described in section 2.2.2.

2.2.4 Immersion in Saponin solution

An extract was prepared by boiling three tablespoons of saponin leaves, stems and roots with 750mls of distilled water for 30 minutes (3). The mixture was cooled and filtered to collect the extract. This was diluted with distilled water to give a 20% solution. The extract was used within 48 hours of preparation, since it became mouldy after this period if not stored in a refrigerator. Textile samples were immersed in baths of the concentrated and 20% extract solutions for 15 minutes and then either dried or rinsed before drying as described above in 2.2.2.

2.2.5 Running rinse

Samples were mounted along the upper edge of a flat, glass plate using electrical insulating tape. A cold water tap was set to deliver 1 litre of water per minute and the plate fixed at a 60°C angle directly below the tap. The water was allowed to run over each sample for 15 minutes. Samples were dried on the glass plate at room temperature. The procedure was repeated with the tap delivering 6 litres of water per minute.

2.3 Methods of Assessment

The test methods described below were applied to all samples.

2.3.1 Optical Methods

All samples were examined visually and using an Olympus binocular microscope at magnifications up to x 128.

Examination of the treated samples by eye showed no changes in colour, dimension or texture were caused by washing, except in the case of filled, high density Japanese silk. This softened on contact with water and expanded in the direction of the warp. Disturbance of the warp fibres resulted in a loss in planarity of samples and an increase in surface area and was probably caused by swelling of the gelatin filler.

Slight matting of the warp and weft fibres of linen was observed after immersion in both standard washing solution and Synperonic N. The wefts of the wool samples were slightly roughened by exposure to the running rinses.

Under the optical microscope, cotton and silk fibres appeared unaffected by aqueous treatments.

2.3.2 Fibre Density

The number of warps and wefts occupying a square centimetre (fibre density) were counted for each sample before and after treatment.

An analysis of variance on all the data indicated that wefts of all textiles were affected more than warps by aqueous treatments. This is expected since woven textiles tend to be weaker in the direction of the weft than in the direction of the warp threads. Warp and weft fibre densities varied sympathetically, that is when the number of warps per centimetre decreased, the weft densities increased by a similar value. Greater variation in fibre densities after treatments was displayed by the closer woven silk and linen than by the looser woven cotton and wool. Analysis of variance indicated that a change in fibre density greater than one unit was significant. This was only observed for silk which showed variations of between 1 and 6 after treatment.

The largest effect was as a result of immersing high density silk for one hour in the standard textile washing solution. The density of the warps decreased and that of the wefts increased by an average of 3 threads per square centimetre, or 7%. Since the filled silk was not affected to the same extent, it may be concluded that the gelatin filler acted as a support for the fibre threads. Wool was the most dimensionally stable sample after aqueous immersion, compression in the direction of the wefts occurring after treatment with Synperonic N and 1 litre per minute running rinse. In addition, expansion in the direction of the warps occurred after treatment with the saponin.

2.3.3. UV-reflectance spectroscopy

Colour change on washing was determined by measuring the ultraviolet reflectance spectrum of each sample before and after treatment using a Perkin-Elmer 551S UV/visible spectrophotometer with a reflectance sphere attachment. The percentage reflectance of light at 500nm, the wavelength of maximum reflectance, was measured for each sample. The washing power was calculated using equation (1) and was used as a measure of the effect of aqueous immersion on the optical properties of the samples (4). The results are shown in Table 1.

$$\text{Washing power (\%)} = \frac{RA - RB}{RB} \times 100 \quad (1)$$

Where RA = % reflectance of sample after treatment
and RB = % reflectance of untreated sample

Cotton, wool, linen and filled, high density silk were brightened to the greatest extent by treatment with standard textile washing solution. Immersion in tap water and saponin solution were most effective on Japanese silk.

Since all test pieces were clean, the ability of a particular treatment to cause darkening or brightening may be attributed to the accumulation along the fibres of either cleaning agent or salts from hard water. This would affect the reflective properties of the fibres.

The period of immersion was also a significant factor in the effect of a treatment on the reflectance of a textile. A 30 minute immersion in a bath of any of the cleaning agents prepared with distilled water gave the optimum brightness for each treatment. Longer immersions resulted in a reduction of reflectance for all textile samples. This may be attributed to the further penetration of water and cleaning agents into the fibres, resulting in disruption and roughening.

2.3.4 pH

The pH of all washing solutions and wash liquors was measured before and after immersion of the samples using a Pye-Unicam Model 291 Mk2, pH meter.

The pH of rinse liquors after treatments involving tap water stabilised at a higher pH than those prepared in distilled water. This suggested that cleaning agents prepared with tap water were retained by the textile fibres for a longer period than those containing distilled water.

2.3.5 Conductivity

The conductivity of all washing solutions and rinse liquors were measured at 25°C using a Kent WPA CM D400 meter both before and after immersion of the samples. The results showed similar trends to those of the pH measurements.

2.3.6 Viscometry

Viscosity measurements were made on all samples after completion of wash and rinse treatments, and on untreated controls. Textiles were cut into 2mm squares to facilitate solution and 0.053g was weighed into a sample tube. Cuprammonium hydroxide (20mls) (for silk) or Cadoxen (20mls) (for cotton, linen and wool) were added by pipette, and the tube was magnetically stirred until a clear solution was obtained. Stirring times were 15 minutes in the case of silk and three hours for all other samples.

The solutions were filtered through Whatman glass fibre filter and heated to 25°C in a water bath. A size C, U-tube viscometer was charged with the solution and retained in a water bath at 25°C for 10 minutes before measuring the viscosity of the solution. The viscometer was calibrated with a 65% aqueous solution of glycerol at the working temperature (5). The fluidity of the solutions was calculated from the flow time.

Fluidity is defined as the reciprocal of the viscosity of a solution. A high fluidity represents a lower molecular weight and indicates disruption to fibres. A low fluidity represents a high molecular weight indicating that little disruption has occurred. Fluidity has been adopted as a standard method of recording viscosity measurements in the textile industry.

Fluidity was calculated in accordance with BS 2610, employing equation 2.

$$F = \frac{c^1}{t - k^1} \quad (2)$$

where $c^1 = c/d$ and $k^1 = k/t$,

F = fluidity in poise⁻¹ (P^{-1}) (1 poise = 0.1 Nsm⁻²)

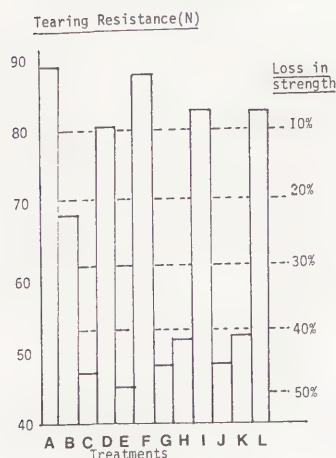
k = kinetic energy correction constant = 151.95

c = the viscometer constant = 852.74

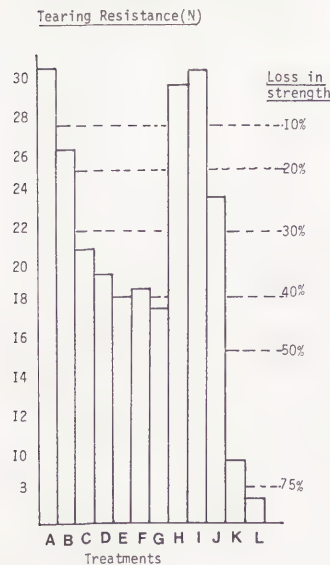
d = density of solvent used = 0.94 gcm⁻³ for cuprammonium hydroxide and 1.06 gcm⁻³ for Cadoxen at 25°C.

t = time required for a test solution to flow through the viscometer (s).

FIGURE 1
TEARING RESISTANCE OF COTTON
AFTER AQUEOUS CLEANING TREATMENTS



TEARING RESISTANCE OF SILK
AFTER AQUEOUS CLEANING TREATMENTS



KEY

- A=Untreated
- B=Distilled Water(5mins.)
- C=Distilled Water(overnight)
- D=Tap Water(5min)
- E=Tap Water(overnight)
- F=Std.Textile Washing Soln (distilled water)
- G=Std.Textile Washing Soln. (tap water)
- H=Synperonic N solution
- I=Saponin extract
- J=Dilute Saponin
- K=1 litre/min. rinse
- L=6 litre/min. rinse

The fluidity of all treated cotton samples was between 5 (control sample) and 10, similar to that of normal scoured and bleached cotton, that is undamaged cotton (6). The highest fluidity was as a result of treatment by Synperonic N, closely followed by saponin, suggesting that these treatments damaged the cotton fibres more than the other cleaning agents. The lowest fluidity was measured after treatment with a 1 litre per minute running rinse. Increasing the rate of flow of the rinse by a factor of 6 caused only slightly more damage to the cotton fibres.

The range of fluidity for treated wool was 17.8 (control sample) to 24.6. The 6 litre per minute running rinse was the most damaging treatment. Immersion in tap water, standard textile washing solution and dilute saponin had similar less damaging effects on wool. Synperonic N produced the smallest increase in fluidity, suggesting it to be the least damaging cleaning agent for this material.

The range of fluidity for linen was 4.9 (control sample) to 6.5, which indicated that immersion in the aqueous washing solutions caused little reduction in molecular weight (6). The highest fluidities were measured after the 1 litre and 6 litres per minute running rinses.

The range of fluidity values for Japanese silk was 14.1 (control sample) to 18.4, most of the treatments giving fluidities below 15 which is the upper limit for normal spun silk threads (6). Treatment with the 6 litres per minute running rinse gave the highest fluidity, followed by the standard textile washing solution. This indicates that these two treatments reduced the molecular weight by approximately 7%. The remaining treatments gave fluidities similar to that of untreated silk suggesting that they caused negligible damage to fibres.

The filled and unfilled high density silks showed similar trends in fluidity although the results from the filled sample may have been affected by the gelatine filler dissolving in the cuprammonium hydroxide. The values range from 4 to 12. Only treatment by standard textile washing solution resulted in a fluidity higher than the upper limit expected for undamaged silk, followed by the 6 litre per minute running rinse. Based on fluidity measurements, distilled water and saponin were the least damaging treatments.

2.3.7 Tearing resistance

The maximum tearing resistance is defined as the highest local peak force developed when a tear is prolonged under the condition of the test.

The method used was an adaptation of BS 4303:1968 'Determination of the resistance to tearing of worn fabrics by the 'wing-rip technique'' (7). Samples of treated and untreated textiles 2 cm x 7 cm were pre-conditioned at 65% RH and 20°C for four hours prior to testing. A 3mm cut across the warps was made halfway down the longest edge, the sample clamped into a JJ Lloyd Tensile Tester, and a load applied until the tear extended across the width of the fabric. Six samples of each treatment were tested for all textiles.

The results are shown in Figure 1.

The results suggested that silk was weakened more by the aqueous immersion and running rinse treatments than non-silks. The non-silks were affected least by treatment with the standard textile cleaning solution and Synperonic N, while saponin and Synperonic N had least effect on the tearing resistance of the silks. Short soaking times in distilled water-based solutions caused less damage than soaking in solutions prepared with tap water.

3. Conclusions

The effect of cleaning by immersion in aqueous washing baths, or exposure to flowing water was found to be dependent on the properties of the textile to which it was applied. For example, closer woven textiles showed greater variation in fibre density than looser woven samples, wool being the most dimensionally stable.

The period of immersion was also a significant factor. Thirty minute soaks resulted in maximum percentage reflectance values for all samples. Longer soaking periods caused maximum darkening of the fibres and noticeable weakening. Incomplete rinsing also contributed to weakening of all textiles since residues of the cleaning agents accumulated between the fibres thus decreasing the flexibility of the sample.

Summarising all the results obtained, it may be concluded that silk and linen were less amenable to aqueous washing than wool and cotton. Standard textile washing solution was the most efficient and least damaging washing agent for cotton, linen and wool. It was readily rinsed from the samples and gave the highest washing power, while causing a minimal reduction in tearing resistance. Short immersion (less than 30 minutes) in saponin solution was found to be the most suitable washing process for silk, resulting in a high washing power while maintaining fluidity and tearing resistance values similar to those of untreated material. A 6 litres per min running rinse proved the most disruptive treatment for all textiles evaluated.

Based on these results a flow chart for selection of washing technique has been prepared in conjunction with a textile conservator. The flow chart is presented in Appendix I.

The processes evaluated are to be repeated on old samples of cotton, wool linen and silk and the results compared with those obtained to date. Soiling agents may be introduced to the textiles and the efficiency of suitable washing solutions investigated. Solvent cleaning is also to be examined in the longer term.

Acknowledgements

I would like to thank Mrs S M Bradley for her advice, Ms M E A McCord and Ms A Rae for providing samples and sharing their considerable experience of cleaning textiles, Dr M Leese for her help with statistical treatments, and to Mr W A Oddy for encouragement to publish.

MATERIALS

'Shirley' Cuprammonium hydroxide

BDH Limited
P O Box 15
Freshwater Road
Dagenham
Essex
RM8 1RF
Tel: 01 597 7591

Synperonic N (nonylphenol
ethoxylate in aqueous solution
BDH Limited
(Address as before)

Cadoxen Reagent
Koch-Light Laboratories Ltd
37 Hollands Road
Haverhill, Suffolk, CB9 8PU
Tel: 0440 702436

Saponin roots, leaves and stem

Neal's Yard Apothecary
2 Neal's Yard
Covent Garden
London WC2

Cotton, wool, linen and Japanese silk
John Lewis & Co Ltd
Oxford Street
London W1
Tel: 01 629 7711

High Density Silk bought from Japan and supplied by Eastern Pictorial Art Section.

References

1. Personal Communication, Thames Water Board, London Borough of Camden.
2. Landi, S., 'The Textile Conservator's Manual,' Butterworth (1985).
3. Maxwell-Hudson, C., 'The Natural Beauty Book', Macdonald and Jane's. London 1976.
4. Vogtman, W., 'A New Method for Evaluating the Washing Power of Washing Agents for Cotton Fabrics', JAOCS, Nov 1981 pp 1012-1019.
5. BS 2610:1955 Fluidity of cottons, rayons and cellulose acetate (in cuprammonium hydroxide solution). Handbook 11:1974 Section 5.
6. Garner, W., Textile Laboratory Manual Vol. 5, Third Edition, London Heywood Books, (1967).
7. BS 4303:1968 Determination of the resistance to tearing of woven fabrics by the wring-rip technique. Handbook 11:1974 Section 4.

TABLE I

Washing Power of Cleaning Agents on Undyed, Modern Textiles.

Washing Agents	Washing Power (%)				
	Cotton	Wool	Linen	Japanese Silk	High Density Silk
Distilled Water	5.1	3.2	0.2	2.4	5.3
Tap Water	5.4	5.0	1.6	5.6	3.8
Std. Textile Washing Solution	9.0	9.0	2.0	4.5	29.6
Synperonic N	5.6	5.6	0.3	3.4	25.3
Saponin Solution	6.4	6.4	-6.0 ¹	-1.2 ¹	27.8
Dilute Saponin Solution	0.8	0.2	-4.8 ¹	9.8	25.3

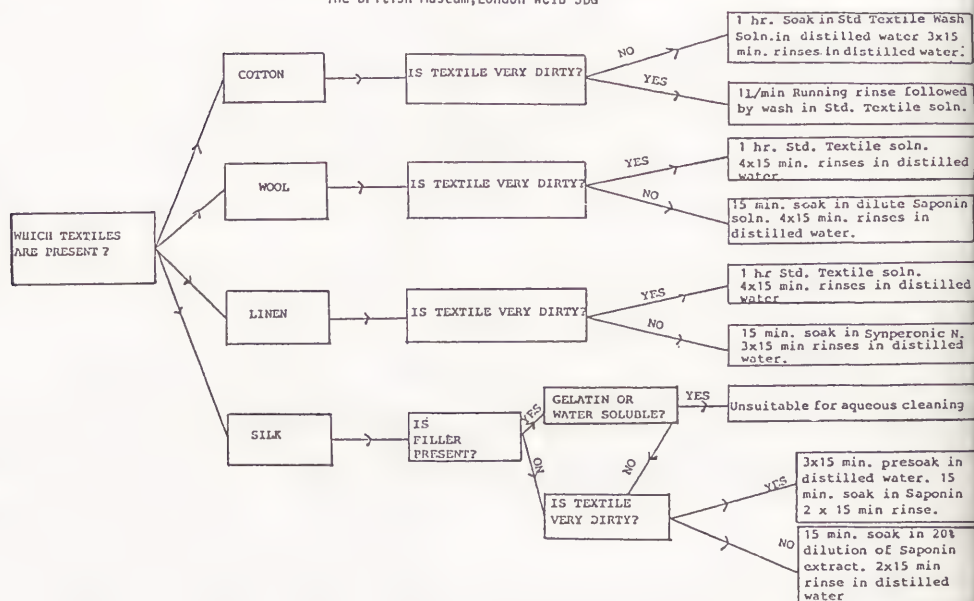
1. Negative values indicate darkening of the sample after washing.

APPENDIX 1

Flow Chart for Selecting Methods of Washing Textiles by Aqueous Immersion

Allison Rae and Yvonne Shashoua, Department of Conservation

The British Museum, London WC1B 3DG



Working Group 10

Stone

Matériaux pierreux

ABSTRACT

The Cerro Colorado area presents a distinct weathering pattern of its red sandstone resulting in the formation of open caves and, in some instances, honeycomb alteration. The area is important because the overhangs and shelters formed by this weathering were used as background for the rock-paintings carried out by the early indigenous inhabitants.

A hypothesis of the mechanisms that give origin to these deterioration patterns is discussed.

KEYWORDS

Open cave formation, honeycomb weathering, salt crystallization, sandstone, wind erosion.

PRELIMINARY STUDIES OF DETERIORATION PATTERNS AT CERRO COLORADO, ARGENTINA: OPEN CAVE FORMATION AND HONEYCOMB WEATHERING

A. Elena Charola,
ICCROM
13, Via di San Michele
I-00153 Rome
Italy
(Permanent address: Murature 830, 1642 San Isidro, Argentina)

Johannes Weber*)
Institut für Silikatchemie und Archäometrie
Hochschule für angewandte Kunst
Salzgries 14/1
A-1013 Vienna
Austria

Erica Bolle
Comisión Nacional de Museos y de Monumentos y Lugares Históricos
Avda. de Mayo 556
1084 Buenos Aires
Argentina

Introduction

The Cerro Colorado area, circumscribed by the Archaeological and Natural Park of Cerro Colorado, Córdoba, Argentina, is formed by several hills and hillocks of red sandstone from which the main hill gets its name. The Park is about 15 square kilometers in area and is located in the north-northwest corner of the Province of Córdoba, in the center of the Republic.

These hills have weathered unevenly giving rise to the formation of overhangs and open caves (see Fig. 1), which were used and decorated with paintings by the local indigenous inhabitants. These rock-paintings predate the arrival of Columbus but were continued till after the Spanish conquerors colonized the area. Further information on the rock-paintings is given elsewhere (1).



Figure 1: A view of the Cerro Colorado showing the formation of overhangs and open caves.

In some parts, honeycomb weathering developed on the walls of these open caves.

Description of the Rock

The sandstone forming these hills corresponds to the permian-carboniferous Cerro Colorado formation (neopaleozoic era (2)). The formation is made up of grey to red sandstones of fairly uniform fine to medium granulometry, but which in some places turns coarser and forms conglomerates. The sandstone is composed of quartz with only minor amounts of feldspar (3). The nature of the binding material varies between silicic and calcareous, a notable amount of kaolinite seems always to be present.

The sedimentation planes of the formation run fairly horizontally.

The alternating sedimentation pattern of sandstones of different hardness, cohesion and texture, gave rise to the formation of overhangs or open caves (4). The variation in the physical characteristics mentioned could be attributed in part to the nature of the binding material within the stone.

*) Author to whom correspondence should be addressed

The quartz grains in the sandstone are partially to totally covered with clay minerals, mostly well crystallized kaolinite. The large grain size of kaolinites in pores implies their growing under the influence of more or less hot solutions. On the other hand, the presence of clay could have favoured to some extent the pressure solution process and the formation of secondary quartz (5). Iron and manganese oxides/hydroxydes are also present.

On weathering the sandstone tends to form a crust of several millimeters up to half a centimeter that is deeper, -redder-, in colour than the stone itself. The mechanism of this type of rind formation could be attributed to the migration of oxidized iron together with a silica welding process. The crust is so compacted that it will break through individual quartz crystals rather than through grain boundaries.

Rock Deterioration

The deterioration of the stone is affected by two main factors: the presence of water percolating through it and the effect of wind. The effect of the water is twofold: it can solubilize the binding material, and it can carry soluble salts in solution.

The dissolution of binding material, be it the secondary quartz or the calcareous binder, will decrease stone cohesion decreasing its mechanical resistance and increasing its porosity. Obviously, those areas where the sandstone has a calcitic binder will be far more susceptible to deterioration than those with a silicic binder, due to the higher solubility of calcium carbonate.

The crystallization of soluble salts will occur preferentially in areas of higher porosity (6). The two main salts present in the Cerro Colorado area are: calcium sulphate, which is found ubiquitously throughout the area as gypsum, and sodium sulphate, which causes most damage.

In those shelters where sodium sulphate is present, extreme deterioration is found. This is evidenced by severe powdering and/or flaking of the stone surface (see Fig. 4 in Ref. 1). Gypsum, though causing a similar kind of surface deterioration, does not produce it to the same degree.

Where water runs over the surface of the stone it tends to leave a whitish gypsum deposit. In some places this is combined with reprecipitated calcium carbonate.

Discussion and Conclusions

The mechanism of open cave formation can be said to occur in the following manner: water percolates through the sandstone, solubilizing the binding material between the quartz grains. The stone is thus physically weakened and more susceptible to the mechanical erosion caused by wind. Strata of sandstone that contain a calcareous binder will be more susceptible to the formation of open caves than those with silicic binder.

If the water percolating through the stone carries a soluble salt, either sodium sulphate or calcium sulphate, the crystallization of these salts will take place preferentially in areas of higher porosity, i.e., those areas that have already lost part of their binder due to water percolation. Therefore, the deterioration of those areas will be accelerated due to the presence of soluble salts. The presence of sodium sulphate increases the rate of deterioration significantly. This is due to the nature of this salt which can crystallize and recrystallize, upon changes of thermohygrometric conditions, as a hydrate or an anhydrate.

Honeycomb weathering has only been observed locally on two hills: Cerro Condorhuasi and Cerro de la Conga. In both sites this weathering occurs on the north-east side of the hill. In the case of the Cerro Condorhuasi, the honeycombing occurs at intermediate level overhangs, while at the Cerro de la Conga it occurs in a cave at the base. This height level difference is possibly due to localized wind eddying effects. The deterioration can be attributed to the strong north wind, which usually blows in the hot and dry season. It is worth mentioning that this weathering occurs in sandstone strata with silicic binder.

Within the alveoles formed by this weathering (see Fig. 2), a surface deposit or crust is found (see Fig. 3). This crust is formed by gypsum and is covered on the upper surface by amorphous silica (see Fig. 4), and on the underside by chalcedony-like formations (see Fig. 5). It is evident that the dissolved silicic binder is reprecipitated jointly with the calcium sulphate dissolved in the percolating water. Once the crust forms, the reprecipitation of chalcedony can occur underneath it following a recrystallization mechanism similar to that occurring in stalactite formation (7, 8).

The formation of honeycomb weathering has been attributed to several causes: wind erosion combined with the presence of soluble salts (9, 10), together with chemical weathering (11, 12), or in conjunction with microbial action (13), or marine boring organisms (14).

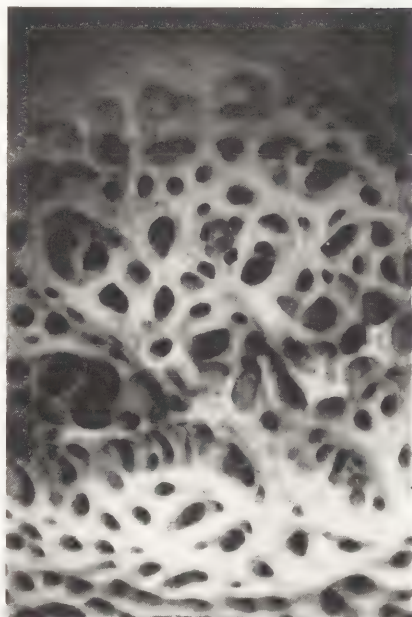


Figure 2: A close-up view of the honeycomb weathering found at Cerro Condorhuasi.

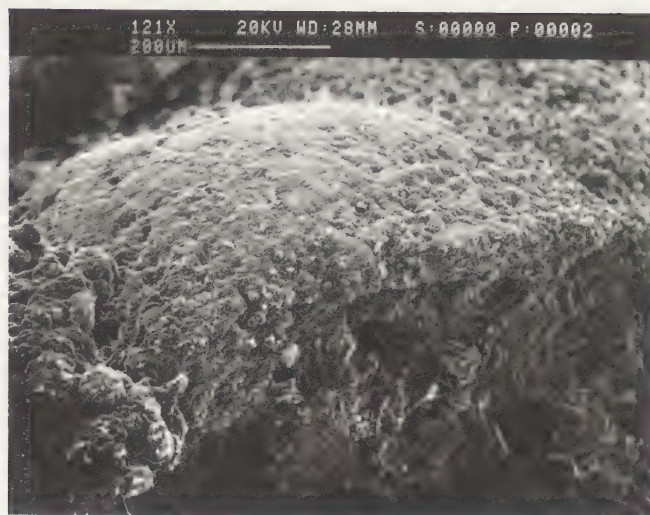


Figure 3: SEM photomicrograph of the fractured cross-section of the crust that lines the interior of the alveoles in the honeycomb weathering found at Cerro Condorhuasi. The picture shows the outer part of the crust formed by a hard rind of gypsum and amorphous silica.

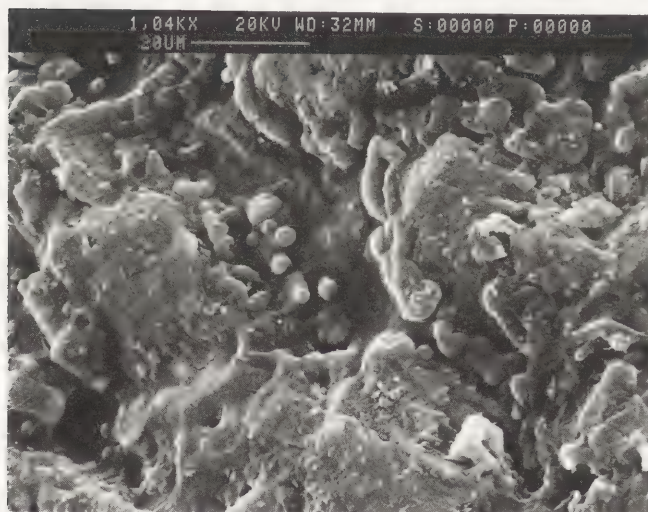


Figure 4: SEM photomicrograph of the outer surface of the same crust showing the amorphous silica deposit on the underlying gypsum.

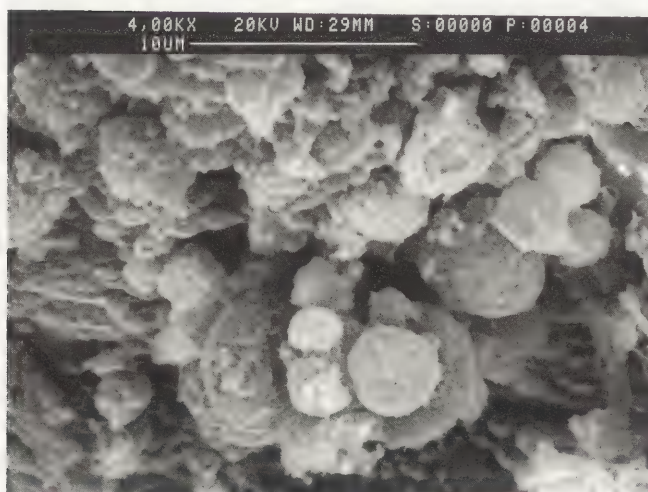


Figure 5: SEM photomicrograph of the underside of the crust from Figure 4 showing chalcedony-like silica structures.

The actual shape of the alveoles in this type of weathering has been attributed to the internal structure of the stone, i.e., porosity differences which would cause preferential redeposition of binding material, thus strengthening some areas while weakening others (15). It is conceivable that the redeposition of binding material could follow a Liesegang ring pattern. Thus concentric rings could be formed of alternating hard and weak areas. The hard areas would be formed where the less soluble material, silica or iron and manganese oxides/hydroxides is deposited. The weak areas would form where the more soluble salts, such as gypsum, are enriched, or where the binding material has been partially dissolved. The superposition of several of these ring patterns could give rise to the observed honeycomb weathering. The silicified gypsum deposit lining the interior of the alveoles appears to substantiate this hypothesis.

It would appear therefore that honeycomb weathering is the combination of two factors: a redistribution of the binding material within the stone, forming alternating indurated and weakened zones, and a dry, strong wind producing rapid evaporation. Soluble salts appear to play a lesser role than in the formation of open caves.

The redeposition of binding material can only occur in the presence of water. It has been observed that honeycomb weathering forms on surfaces that are neighbouring to areas over which water flows. Where water flows frequently, if not continuously, algal growth can be observed (see Fig. 2) and it is possible that this growth protects the stone from wind erosion. Areas close to seepages or flowing water will be damp without being wet. Thus, liquid water will only be found lining the capillary walls of the stone. This may be sufficient to produce the dissolution of the binding material, and provide the right conditions for its migration and redeposition in a periodic pattern. The damp stone will be softer than the dry stone and therefore more susceptible to wind erosion. The clay content of stone may play an important role in maintaining moisture within it.

Summarizing, the formation of open caves appears to occur due to the effect of wind over areas where the stone has been weakened by partial loss of its binding material and through the mechanical damage produced by repeated soluble salt crystallization.

Honeycomb weathering forms through a similar mechanism but only on sites where certain humidity conditions are fulfilled. These are necessary to produce the pattern of alternating weakened to strengthened stone, following dissolution or redeposition of the binding material, thus giving rise to the alveolar shape in this deterioration.

References

- (1) E. BOLLE, M. WYPYSKI and A.E. CHAROLA, "Preliminary Study of the Rock Paintings at Cerro Colorado, Córdoba, Argentina" (Paper submitted for publication at the Ninth Triennial Meeting of the International Council of Museums Committee for Conservation, Dresden, 1990).
- (2) H.N. LUCERO MICHAUT, "Sierras pampeanas del norte de Córdoba, sur de Santiago del Estero, parte oriental de Catamarca y ángulo sud-este de Tucumán" (Pampean Hills of North Córdoba, South Santiago del Estero, Oriental Part of Catamarca and South-east Angle of Tucumán) in *Geología Regional Argentina Vol. 1* (Córdoba: Academia Nacional de Ciencias, 1979) 322.
- (3) H.N. LUCERO MICHAUT, "Contribución al Conocimiento Geológico del Cordón Oriental de la Sierra Norte entre Simbolar y el Limite con Santiago del Estero" (Contribution to the Geological Understanding of the Oriental Strand of the Sierra Norte between Simbolar and the Boundary with Santiago del Estero), *Boletín de la Asociación Geológica de Córdoba* 4, No. 1-4 (1981): 223-235.
- (4) E.J. METHOL, "Descripción Geológica de la Hoja 18i, Deán Funes, Tulumba, Córdoba" (Geological Description of the Sheet 18i, Deán Funes, Tulumba, Córdoba), in *Carta Geológica Económica de la República Argentina 1:200.000. Boletín No. 88* (Buenos Aires: Dirección Nacional de Geología y Minería, 1958).
- (5) A.V. CAROZZI, *Microscopic Sedimentary Petrography* (Huntington, N.Y.: Robert E. Krieger, 1972), 22-29.
- (6) L. BINDA and G. BARONIO, "Alteration of the Mechanical Properties of Masonry Prisms due to Ageing," *Proceedings of the Seventh International Brick Masonry Conference* (Melbourne, 1985), 605-616.
- (7) S.Z. LEWIN and A.E. CHAROLA, "Aspects of Crystal Growth and Recrystallization Mechanisms as Revealed by Scanning Electron Microscopy," *Scanning Electron Microscopy Vol. I* (1980), 551-556.

- (8) A.E. CHAROLA and S.Z. LEWIN, "Efflorescences on Building Stones - SEM in the Characterization and Elucidation of the Mechanisms of Formations," Scanning Electron Microscopy Vol. I (1979), 378-386.
- (9) J.P. PAULY, "Maladie Alvéolaire. Conditions de Formation et d'Evolution" (Alveolar Decay. Conditions for its Formation and Evolution), in The Conservation of Stone. I, ed. R. Rossi-Manaresi (Bologna: Centro per la Conservazione delle Sculture all'Aperto, 1976), 55-80.
- (10) D. DRAGOVICH, "Weathering of Sandstone Tombstones in a Coastal Environment, Sydney, (Australia)," in The Engineering Geology of Ancient Works, Monuments and Historical Sites, eds. P. G. Marinos and G. C. Koukis (Rotterdam: Balkema, 1988), 853-858.
- (11) J.P. MCGREEVY, "A Preliminary Scanning Electron Microscope Study of Honeycomb Weathering of Sandstone in a Coastal Environment," Earth Surface Processes and Landforms 10 (1985), 509-518.
- (12) P.R. BUTLER and J.F. MOUNT, "Corroded Cobles in Southern Death Valley: Their Relationship to Honeycomb Weathering and Lake Shorelines," Earth Surface Processes and Landforms 11 (1986), 377-387.
- (13) G.E. MUSTOE, "The Origin of Honeycomb Weathering," Geological Society of America Bulletin 93 (1982), 108-115.
- (14) R. PESTRONG, "Tafoni Weathering of Old Structures along the Northern California Coast, USA," in The Engineering Geology, 1049-1050.
- (15) A. SCHMOELZER, "Zur Entstehung der Verwitterungsskulpturen an Bausteinen" (On the Formation of Weathering "Sculptures" on Building Stones), Chemie der Erde 10 (1936), 479-520.

Acknowledgements

The authors would like to thank Prof. E. Gomez Molina of the Universidad de Córdoba, Argentina, for providing the invitation to visit Cerro Colorado which gave origin to this work.

Thanks are also due to the Samuel H. Kress Foundation for their support of the interlaboratory collaboration.

ABSTRACT

Analysis of different samples of the sphinx's rock and the surrounding plateau was carried out. Using X-ray diffraction analysis (XRD), to determine the nature and source of salt which led to its deterioration. The XRD data demonstrated that halite and gypsum salt are naturally occurring minerals in the limestone mother rock of the sphinx. The subsoil water and moisture surrounding the sphinx play an important role in dissolving salts, their migration, and recrystallization at the surface. Stabilization of the existing salts by controlling the effect of water and applying consolidants and water-repellent materials is the best method for conservation of the sphinx.

KEYWORDS

SALT CRYSTALLIZATION, WEATHERING, X-RAY DIFFRACTION, CONSOLIDATION, SPHINX.

STUDY OF SALT PROBLEM IN THE SPHINX, GIZA, EGYPT.

Fatma M. Helmi

Cairo University, Faculty of Archaeology,
Conservation Department, Giza, Egypt.

INTRODUCTION

The Sphinx is one of the marvellous and important Egyptian Antiquities (4th Dynasty 2680-2563 B.C.). It was most probably built during Khafre's reign, who was also the builder of the second pyramid, as well as funerary and valley Temples at Giza, Egypt. The Sphinx represents Hor-akhty or Horus on the "horizon". It has the head of a man (resembling Khafre) and the body of a lion, so as to represent mental faculties and bodily power(1).

The Sphinx was carved from stone originally from the Mokattam formation of Middle to Upper Eocene age at Giza. The Mokattam formation consists of a series of massive limestone beds containing characteristically large foraminifera, the nummulites (2).

The bedrock of the sphinx consists essentially of three portions: (1) Very hard limestone constituting the base of the Sphinx, (2) The body is composed of successive layers of very soft limestone interbedded with thin layers of a comparatively hard limestone and (3) very hard and compact limestone forming its neck and head.

Deterioration phenomena of the Sphinx since its carving are due to many factors: defects in the mother rock, salt crystallization, ambient moisture and subsoil water, wind eddies, ancient gypsum mortar used in the sphinx veneer, and arid climate (3).

The aim of the present work is to study the salt problem and to find a solution for the Sphinx's conservation.

EXPERIMENTAL**Material Studied**

Twenty samples were obtained representing the different beds of the Sphinx's eleven samples from Giza plateau formation surrounding the Sphinx, and four samples from ancient mortar used in the construction of the Sphinx's veneer.

X-Ray Diffraction Analysis

Each sample was ground in an agate mortar to a fine powder, pressed into the specimen holder, and then mounted in a Philips X-ray diffractometer. The operating conditions were: generator: Cu K α radiation (1.5418 Å) with Ni filter, 36 KV, 16 mA current tube; goniometer: Scanning velocity 2°/min., divergent slit 1°, receiving slit 0.2, scattering slit 1°; proportional counter: H.V. supply 1780 volt, chart velocity 10 mm/min°; pulse height analyser: attenuation 3, lower level 3.30, window 4.30; ratemeter: counts/sec. 2×10^2 , time constant 2.

RESULTS**Sphinx's Rock**

Samples from different layers constituting the sphinx from its base, body, and head were analysed. X-ray diffraction data showed that the sphinx's rock consists essentially of calcite and minor or trace amounts of halite, gypsum, and quartz (see Table -I). Major i.e. more than 60%, minor i.e. from 10-40% and trace i.e. < 10%. In some layers the x-ray diffraction patterns showed the existence of clay minerals.

Plateau Formation Surrounding The Sphinx

The succession of plateau formation surrounding the sphinx is not complete. The aim of analysing these samples is to compare them with those of the sphinx's rock. The source of salt is either a natural component in the rock, or from material used in the veneer's construction. X-ray diffraction data showed the existence of halite and gypsum salts in the plateau formation (see Table-II). The concentration of these salts is high at the surface

Ancient Mortar

Different samples of ancient mortar used in the construction of the Sphinx's veneer were analysed. X-ray diffraction data showed that it consists essentially of gypsum and minor or trace amounts of quartz and halite.

DISCUSSION

It is obvious that the salt problem in the sphinx is serious, as it is the main cause of its deterioration, in addition to other factors. The problem is complicated by the existence of halite NaCl and gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ evaporite minerals as natural constituents in the Sphinx's mother rock. There is a conjunction between the salts present in the sphinx's layers and the degree of deterioration. This can be easily seen from differential weathering in its body, as the depressed rock layers are more weathered than those extending outwards. The more deteriorated portions contain more halite and gypsum salts, are friable, and have different physical properties.

During the time of formation of the sphinx's limestone, silt and clay particles settling from the oceanic water became incorporated in the limestone. The extremely small size of these particles and the calcareous test which are mostly unfragmented suggest that this limestone must have formed from the calm oceanic waters which also enabled the precipitation of the evaporites halite and gypsum (4).

Salt normally concentrates on the surface of a rock or wall. The crystallizing system requires a substrate, i.e. stone, wall painting, plaster, or mortar. This substrate becomes more or less saturated with a salt solution and crystals form on the surface which is in contact with the surrounding air (5). In the case of the sphinx, the halite and gypsum salts are present in the mother rock. The subsoil water and ambient moisture supply the limestone with water. The sphinx is situated in a basin which led to the accumulation of subsoil water beneath it. Situated in an arid desert climate, the sphinx is surrounded by a heavy fog in the early morning, which is transformed into water droplets at the surface. A salt solution is formed on the rock; then the recrystallization of salt which occurs at the surface results in the deterioration of the surface layers of the sphinx. Analysis of the surface layers of the sphinx. Analysis of the underground water beneath the sphinx showed that it contains the following elements in ppm: 62 Ca, 30 Mg, 61 Na, 20 K, 250 HCO_3 , 117 Cl, and 65 SO_4 (6). The relatively high concentrations of Na, Cl, and SO_4 are due to the penetration of water from the surface strata which has a high salt concentration.

Whisker growth from salt solutions on porous substrates is a known phenomenon. One characteristic growth condition is an exposure to a slightly supersaturated solution. This growth condition also requires a very low water content of the porous substrate, a very low solution supply from the interior of the wall, and a very slow evaporation rate which is often controlled by seasonal humidity variation in air (5). These phenomena can be observed on the eastern side of the sphinx. In contrast to the whisker growth, crust formation requires a comparatively high solution supply, and a very humid or wet wall surface (5). Salt crust formation can be observed on the northern side of the Sphinx. By changing environmental conditions, transformations in the crystallized salt may take place, such as aging, dissolution, and recrystallization, which leads to efflorescence of soluble salts.

The Sphinx lies on the east-west line. The effect of sun-rays is very important in the salt crystallization process. The sun rises from the east, in front of the sphinx, and then rotates to its southern side. While its northern side is the least exposed to sun, it is more wet due to the migration of salt solutions to the lower temperature side and the slight inclination of the strata in this direction. The fallen part of the Sphinx's Veneer was at its northern side, which is the more deteriorated one.

Application of siloxane on limestone samples from the Giza plateau surrounding the sphinx was carried out to accomplish conservation of the sphinx.

The physical properties of the samples were determined before and after impregnation. Artificial weathering of the samples by exposure to U.V. radiation, and wet-dry cycles gave satisfactory results. The author is currently undertaking research in this field.

CONCLUSION

The most suitable approach to salvage the sphinx is to stabilize the salts present in the rock. To minimize the dissolution of halite and gypsum salts, their migration, then inhibit recrystallization of these salts at the surface i.e. inhibit Sphinx's deterioration. This can be achieved by controlling access to moisture, by the application of consolidants and water-repellent materials such as derivatives of silane. The moisture content in the sphinx rock will assist the polymerisation process to take place, and protect the sphinx from deterioration. In this case salt will act as a binding material between the limestone grains.

REFERENCES

1. Z.Iskander and A. Badawy, Brief History of Ancient Egypt (Cairo: Madkour press,1965), 40-41.
2. R.Said, The Geology of Egypt (Elsevier Publishing Co.,1962) 98.
3. S.A. Saleh , " Study of Deterioration Factors of stone of the sphinx", A report presented to General Committee for study of Restoration Project of the sphinx, 1981.
4. K.L. Gauri, " Deterioration of stone of the Great Sphinx ", American Research centre Publ., Egypt.1981.
5. A. Arnold and K. Zehnder, " Crystallization and Habits of Salt Efflorescences on Walls II. Conditions of Crystallization in Proceedings of the 5th Intern.Congress on Deterioration and Conservation of Stone, Lausanne, September 25,1985, Vol.I 269-277.
6. K.Hefni," Study of the underground water in the Sphinx Area", A report presented to Egyptian Antiquities Organization,1982.

Table (I): X-Ray Diffraction data of succession beds of the Sphinx's Rock.

Sample	Identified minerals		
	Major	Minor	Trace
Top(head)	Calcite		Quartz
Headdress	Calcite		Gypsum
"	Calcite		Quartz & Gypsum
Neck	Calcite		Quartz & Gypsum
"	Calcite		Quartz
Body	Calcite		Halite
"	Calcite		Quartz
"	Calcite		Quartz
"	Calcite		Quartz
"	Calcite		Quartz
"	Calcite		Quartz
"	Calcite		Quartz & Halite
"	Calcite		Halite
"(surface)	Calcite	Halite	Gypsum & Quartz
"	Calcite		Quartz
Base	Calcite		Gypsum, Quartz & Halite.
"	Calcite		Halite & Quartz
"	Calcite	Quartz	Halite
"	Calcite		Halite
"	Calcite	Halite	Gypsum

Table(II) : X-Ray diffraction data of succession beds of plateau surrounding the sphinx.

Sample	Identified Minerals		
	Major	Minor	Trace
Top	Calcite		Halite
(Surface)	Calcite		Halite & Quartz
(Surface)	Calcite	Gypsum	
	Calcite & Quartz	Halite	
(Surface)	Calcite		Halite
	Calcite & Halite		Quartz
	Calcite		Halite & Quartz
	Calcite		Gypsum & Quartz
	Calcite		Quartz & Halite
	Calcite		Halite, Gypsum & Quartz
Base	Calcite		Halite & Gypsum

ABSTRACT

All materials change irreversibly their properties under the influence of weather and environment. Carrara Marble loses the cohesion between its crystals and extends its porosity. These changes penetrate completely the sculpture and are an indication of its individual history. Ultrasonic investigations are a good means to measure the decohesion and the extension of porosity in marble. Comparison investigations of originals and copies of Carrara Marble sculptures in the Potsdam Park of Sanssouci and in the Bode Museum of Berlin show that the destruction of original sculptures in the museum is similar to that of the copies in the Potsdam Park of Sanssouci.

KEYWORDS

Carrara Marble
Ultrasonic measurements
Decoherence
Porosity
Decoherence structure
Main wind direction

STRUCTURE CHANGES OF WEATHERED CARRARA MARBLE SCULPTURES AS A FUNCTION OF THEIR DESTRUCTION POSITION

Wolfram Köhler
Staatliche Schlösser und Gärten
Potsdam-Sanssouci
1570-GDR

Introduction

Potsdam-Sanssouci has an important collection of about 500 marble sculptures. Among them are Roman antiques of the first century and 20th century copies of antique sculptures. But of primary interest are 400 Carrara Marble sculptures in the Potsdam Park of Sanssouci of the 18th and 19th century / 1 /. This collection of marble sculptures shows many symptoms of weathering. Structural destruction is the important destructive process associated with erosion, formation of crust and frost blasting / 2 /.

Destructive Processes

There are three stages of destructive processes of Carrara Marble in Central Europe.

The first stage of marble destruction begins already in the quarry as intergranular decohesion between the calcite crystals as a result of thermal tension. Most of the pores are submicropores with a size smaller than 2 nm.

In the second stage the porous system is extended after the transport of marble in the Central European climate. The temperature changes during the transport are greater than were in the country of origin. The marble continues to break, micro- and macro-pores develop, the volume of the pores increases slowly and frost blasting begins at extremely low temperatures.

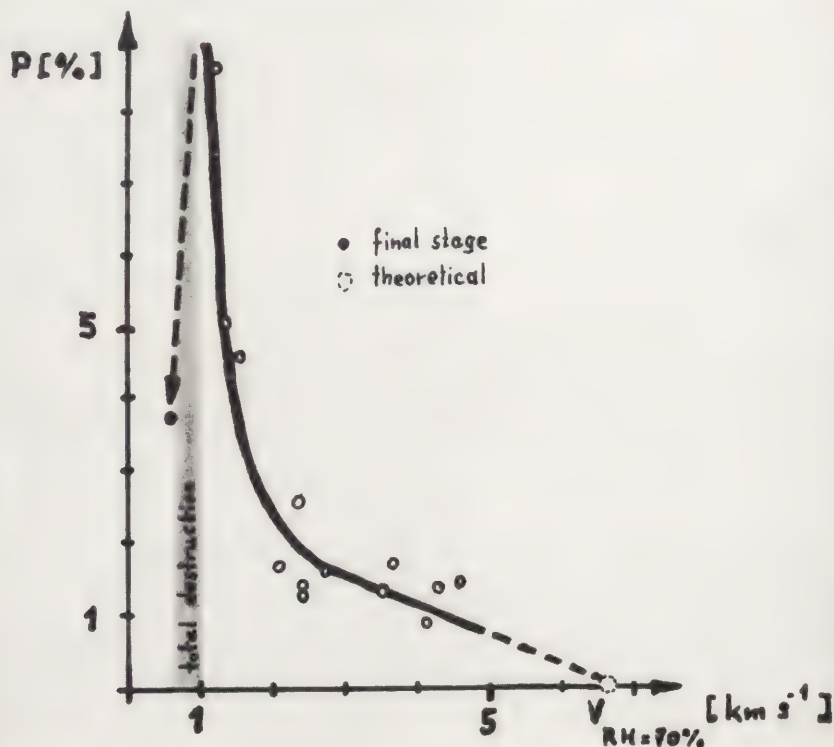
The third stage is the result of frost blasting in the centre and on the surface of the stone. The entire pore system increases rapidly until complete decohesion and finally up to the point when the sculpture falls into ruins.

Ultrasonic Measurements

In Potsdam-Sanssouci more than a hundred sculptures and architectural parts of marble have been investigated in the last two years using ultrasonic measurements.

Ultrasonic measurements are a useful non-destructive method to investigate the destructive processes of Carrara Marble. There is a correlation between ultrasonic velocity v_l and pore volume P in Carrara Marble (see fig. 1).

figure 1: Correlation between ultrasonic velocity v_l (km/s) and pore volume P (%) in Carrara Marble



The preservation condition of Carrara Marble objects can be described in the following manner:

Table I: Stages of destruction due to weathering of Carrara Marble

	condition	ultrasonic velocity (km/s)
fresh marble		4,5 ... 6,5
1st stage	intergranular decohesion	3,0 ... 4,5
2nd stage	extended porous system	2,0 ... 3,0
3rd stage	break off danger (frost blasting)	1,0 ... 2,0
final stage	total destruction	0,6 ... 1,0

Peculiarities of Position

The destructive processes of all Carrara Marble objects are determined by the climatic conditions of their positions. One of the important ensembles in the Potsdam Park of Sanssouci is the "Große Fontainen Rondell" (Great Fountain Roundel). There are 12 sculptures of Carrara Marble made between 1749 to 1764 (see fig.2)

Figure 2: "Große Fontainen Rondell" in Potsdam-Sanssouci



8 sculptures represent antique gods with comparable external stature and size. These 8 sculptures were completely examined.

These are the results of three typical sculptures of this monument.

Two sculptures of them were copied in 1844 and 1904. The original sculptures of "Mercur" and "Venus" have been standing in the Bode Museum in Berlin since 1844 and 1904 respectively (see fig.3).

Figure 3: "Mercur" (since 1844) and "Venus" (since 1904) in the Bode Museum in Berlin



An interesting question is the comparison of the structural changing of originals and copies.

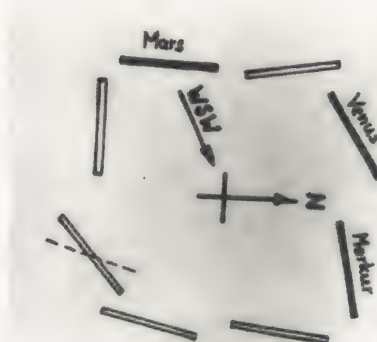
The standard reference for comparison is the sculpture of "Mars" which has been standing in the same Roundel from 1764 to the present.

table II: Originals and copies of Carrara Marble sculptures of the "Großes Fontainen Rondell"

		from	to		in
Mars	original	1764	present	outdoor	Potsdam-Sanssouci
Merkur	original	1748	1844	outdoor	Potsdam-Sanssouci
		1844	present	indoor	Berlin Bode-Museum
Merkur	copy	1844	present	outdoor	Potsdam-Sanssouci
Venus	original	1748	1904	outdoor	Potsdam-Sanssouci
		1904	present	indoor	Berlin Bode-Museum
	copy	1904	present	outdoor	Potsdam-Sanssouci

The outdoor positions of sculptures are determined by the orientation of the sculptures relative to the main wind direction of weathering. The main wind direction in Potsdam is WSW. Every sculpture has an other angle between the main wind direction and the theoretical line "from the left shoulder to the right shoulder" (see fig.4).

figure 4: Theoretical line "from the left shoulder to the right shoulder" relative to the main wind direction WSW of three sculptures in the "Großes Fontainen Rondell"



Results

The ultrasonic investigation shows an interesting structure of the weathered sculptures. Every sculpture has 30 to 40 individual measuring points.

figure 5: "Mars" original of 1748 (photograph and diagram of destruction)

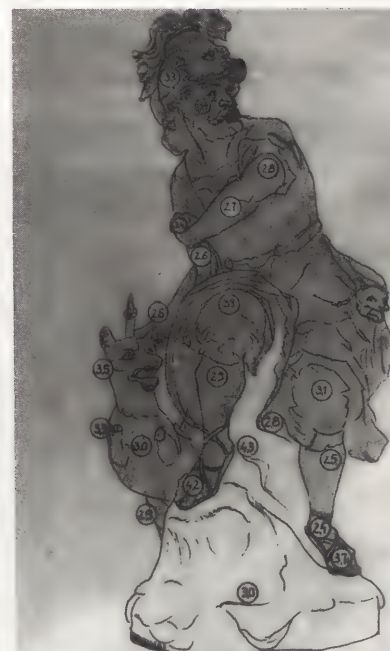


Figure 6: "Merkur" original
of 1748
(photograph and
diagram of de-
struction)



Figure 7: "Merkur" copy of
1844
(photograph and
diagram of de-
struction)

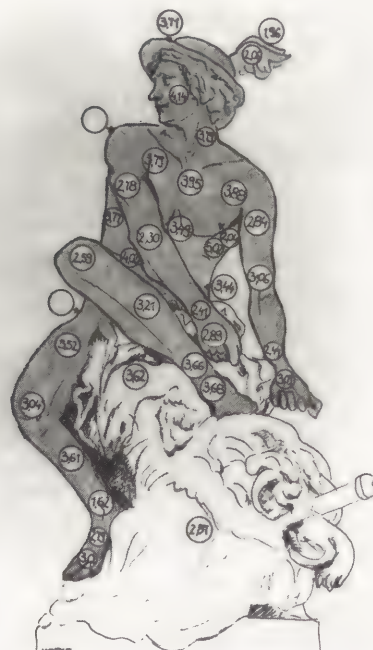


Figure 8: "Venus" original
of 1748
(photograph and
diagram of de-
struction)

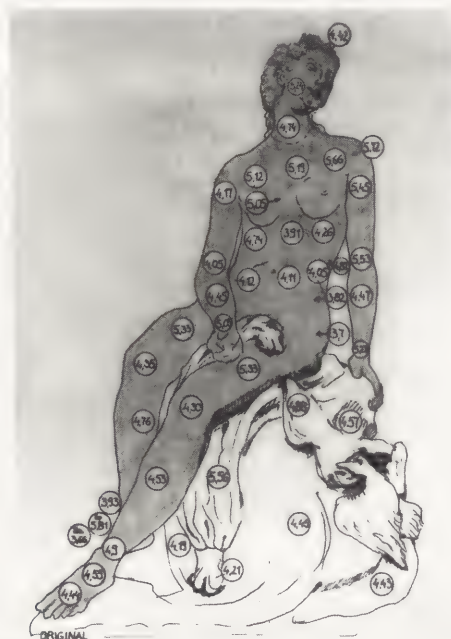


figure 9: "Venus" copy of 1904 (photograph and diagram of destruction)



table III: list of ultrasonic measurements

	Mars original	Venus original	Venus copy	Merkur original	Merkur copy
WSW →					
v 1 (km/s)					
v 1 max	4,3	5,8	5,1	6,2	5,0
v 1 middle					
v 1 min	2,4	3,7	2,3	3,1	1,6

Discussion

The results show that features of intergranular marble destruction can be found in every sculpture with the help of ultrasonic measurements.

The destruction structure of a Carrara Marble sculpture is a permanent reminder of its weathering history.

The destruction structure of the original and the copy of "Venus" are similar.

The weather-side values of sculptures are generally worse than the average of all measurements.

The quality of this effect is affected by the original quality and homogeneity of the marble.

The quality of the "Venus" copy is the worst of all sculptures.

The "Mars" sculpture is weathered more or less from behind and shows this effect of the diameter of all weathered parts of the sculpture.

Exposed to the same weather-side, smaller parts, such as arms and legs, are destructed more quickly than larger parts, such as torsos.

Conclusions

- There is a correlation between the ultrasonic velocity v_l and the pore volume P of Carrara Marble.
- The ultrasonic velocity v_l is a measure of the quality of the original marble and the influence of weather conditions on Carrara Marble objects.
- The destruction structure of a Carrara Marble object is the reminder of its exposition history.
- The present conditions of Carrara Marble objects are dependent on:

Object qualities:

- quality and homogeneity of the original material
- external figures and sizes

Exposure qualities:

- exposition time
 - weather conditions
 - orientation relative to the main wind direction
- The greatest unknown is the quality and homogeneity of the original material.

REFERENCES

- 1 / GORETZKI, L., FÜTING, M.
KÖHLER, W.,
Untersuchungen zur
Korrosion der Marmor-
skulpturen im Park von
Potsdam-Sanssouci,
Bautenschutz und Bau-
sanierung, Heft 3, 1987
 - 2 / KÖHLER, W.,
Preservation Problems
of Carrara Marble
Sculptures in Potsdam-
Sanssouci ("Radical
Structural Destruc-
tion" of Carrara Mar-
ble)
With International
Congress on Deterio-
ration and Conserva-
tion of Stone, Torun
1988
- Ultrasonic Measure-
ments with USME-D by
Elektronik
GÜNTHER KROMPHOLZ, GDR

ABSTRACT

Two bentonites (M and N) and a sepiolite were used for the cleaning of sulphated black incrustations from stonework and for the desalination of marble facing on indoor walls of Venetian monuments. Cleaning efficiency of bentonite N appears to be very good, comparable if not better than sepiolite. SEM-EDX analysis showed the presence of recrystallized gypsum and carbon on the surface of the cleaning pack, detached from the incrustations. Bentonite N and Sepiolite have equivalent desalination properties, as tested by conductimetric measurements.

KEYWORDS

Bentonite, sepiolite, marble, cleaning, desalination

BENTONITE FOR CLEANING AND DESALINATION OF STONES

Lorenzo Lazzarini and Gianni Lombardi
Dipartimento di Scienze della Terra
Università degli Studi di Roma "La Sapienza"
P.le Aldo Moro 5, 00185 Roma

Introduction

The clay minerals sepiolite and attapulgite (synonym of palygorskite) are respectively a hydrated Mg and a Mg-Al silicate with an elongated ribbon structure. This structure has large openings which accommodate several loosely-bound water molecules. This type of structure is responsible for their high sorptive capacities and rheological properties which render them suitable for stone cleaning and de-salting applications.

Hempel (1, 2) first used with success sepiolite for the cleaning of marble and terracotta museum objects from dirt and from thin black incrustation caused by air pollution. Bowley (3) applied large quantities of sepiolite for the desalination of the indoor wall of the London Tower impregnated with sodium chloride. Paleni (4) experimented with attapulgite in the place of sepiolite and obtained comparable results. In Lazzarini (5) is an extended discussion on advantages and disadvantages of these two materials which are widely used by Italian restorers, notwithstanding that sepiolite is imported from Spain and attapulgite from the USA.

Bentonite is a clay with great sorption capacities and rheological properties which render it very suitable for many industrial uses. It is generally composed of over 90% of clay minerals of the smectites group (normally montmorillonite). The types with sodic montmorillonite have much better technological properties than the calcic ones. "Activated" sodic bentonites obtained from the reaction of calco-sodic bentonites with a sodium compound, such as Na_2CO_3 , are also commercially available. These bentonites can give problems for the specific applications here discussed, as sodium carbonate residues may react with the stones during application. A good bentonite should contain very little carbonates and a limited sandy fraction. Bentonite gives no health problems for technicians exposed to its dust. Instead attapulgite with fibers over 5 microns is classified by RPA (Environmental Protection Agency) as probably carcinogenic for man, and by IARC (Int. Agency for Cancer Research) as a possible human carcinogenic substance (6).

Italy is a big producer of bentonite and therefore the suitability of two types of this clay for stone cleaning and de-salting was compared with a sepiolite on the structure of two Venetian monuments.

Materials and methods

Three samples of commercial clays were used for the cleaning and desalination tests:

a - "Sepiolite" is a clay with dominant sepiolite associated with minor amounts of smectite and chert (Table 1). The material used in the experiments is white, fine-grained and is imported from Spain.

b - Bentonite "Atombent A1" is a micronized, slightly activated sodium bentonite with a creamy colour. Its chemical, mineralogical and technological characteristics are in Table 1. Current name in this work: Bentonite M (for micronized).

c - Bentonite "AGB/C P1" is also a whitish sodium bentonite in its natural state, with properties very similar to sample B, but not micronized. Current name in this work: Bentonite N (natural). Both bentonites are from deposits of the Mediterranean area.

The cleaning experiments with the sepiolite and with both bentonites were carried out on the columns of the cloister of the Scuola Vecchia della Misericordia (Venice) where the Pietra d'Istria, a Cretaceous limestone, is covered by thin, uniform, black incrustations. The desalination treatment consisted of 5 successive packs on the Carrara Bardiglio marble facing of the internal left wall of the Church of S. Maria dei Miracoli (Venice) and was carried out with Sepiolite and Bentonite N only. The rheological properties of the micronized Bentonite M were not adequate for this type of use. The stickiness of the poultice impeded an easy application by spatulas; it also tended to swell after application and its homogeneous dispersion in water was difficult to obtain, since aggregates tended to persist. SEM-EDX and XRD were employed to assess the mineralogical and chemical composition of the dirt and of the salts on the marble

	Sepiolite	Bentonite M	Bentonite N
CHEMISTRY			
SiO ₂	52.76	57.98	59.61
Al ₂ O ₃	1.46	25.25	24.34
TiO ₂	0.06	0.22	0.21
Fe ₂ O ₃	0.50	1.96	2.27
FeO	0.26	n.a.	n.a.
MgO	22.52	2.92	2.79
MnO	n.a.	0.02	0.02
CaO	-	0.85	0.82
Na ₂ O	0.20	3.04	2.20
K ₂ O	0.44	0.70	1.13
P ₂ O ₅	n.a.	0.02	0.01
H ₂ O 1000°C	10.53	7.04	6.60
H ₂ O 105°C	11.02	-	-
Total	99.75	100.97	100.00
Moisture	-	10-12	10-12
MINERALOGY			
Sepiolite	92 - 98	-	-
Smectites	0 - 6	94 - 96	92 - 95
Chert	2	-	-
Feldspars	-	1 - 2	2 - 3
Calcite	-	tr	1 - 2
Quartz	-	tr	1
Cristobalite	-	2 - 3	1 - 2
PHYSICAL CHARACTERISTICS			
	Sepiolite	Bentonite M	Bentonite N
Bulk density	-	750/850 g/l	800/900 g/l
Specific gravity			
at 105°C	2.2	-	-
air dry	2.06	-	-
Swelling cap.		40/45 ml/2g	n.a.
C.E.C.meq/100g	26.1	80/85	76/78
Specific surface	330 m ² /g		
Whiteness		83/84	
(BaSO ₄ =100)			
GRAIN SIZE			
< 61 μm	-	100%	97%
< 25 μm	-	100%	63%
< 2 μm	-	28.72%	4.54%

Table 1 Chemical, mineralogical and physical characteristics of the "Sepiolite" and Bentonites used in this work. Data from the literature of the producers.

surfaces and of the removed material on the surfaces of the packs.

The poultice for desalination was prepared by mixing 0.5 kg of bentonite with 0.5 l of distilled water. The packs were removed after dessication and formation of the characteristic craquelure. The progression in the desalination of the marble slabs was checked with a conductimeter after 48 hours immersion and stirring of the dried packs in 3 l of distilled water.

The workability of the materials in the preparation and application of the poultices for cleaning, as well as the aesthetic results were evaluated with the help of the stone restorers.

Results and discussion

Mineralogically, the black incrustations covering the columns of the cloister are composed of gypsum, calcite (presumably of secondary origin) and of traces of quartz. Under the SEM, their morphology is typical of the black scabs formed by interaction of the limestones with the particulate matter polluting the atmosphere of Venice (7, 8). Sometimes, the surface of the columns are covered with a discontinuous net of well-crystallized aggregates of twinned gypsum crystals, resembling the desert roses, in part corroded by dissolution phenomena.

Three diverse cleaning packs - prepared with 0.5 kg of Bentonite M, Bentonite N and Sepiolite mixed with 0.5 l of distilled water - were applied over this surface. Both Bentonites absorb more water than Sepiolite and produce a very sticky poultice with a good adhesive power even on vertical surfaces. The packs were left until spontaneous formation of a craquelure and the consequent breaking down of the mud. This occurred after 4 days from appli-



Figure 1. Comparative cleaning tests on an Istrian stone columns covered by black incrustations. From the top: sepiolite after 4 days; Bentonite N; Bentonite M. Both Bentonites applied for 5 days.

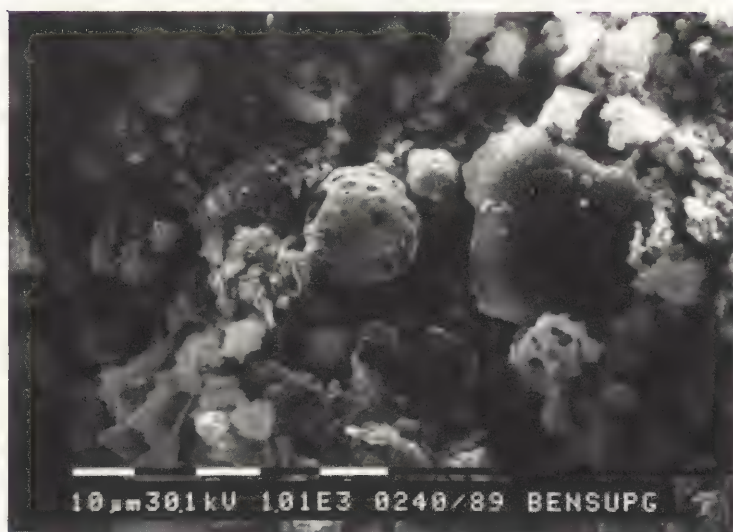


Figure 2 SEM micrographs of the surface of detachment of Bentonite N from the stone. White gypsum aggregate and a round porous carbon particle are clearly visible.

cation for sepiolite; after five days for the bentonites (Fig. 1).

Visual estimates ascertained that one application of Bentonite N produced a satisfactory result, whilst a second pack of both Bentonite M and Sepiolite was needed for a good cleaning.

SEM-EDX analysis of the detachment surface of the Bentonite N pack showed that the well-crystallized gypsum of the black incrustations had been removed and recrystallized in powdery aggregates on the internal clay surface (Fig. 2). On the same surface were also visible the porous carbon particles causing the black colour of the incrustations.

For the desalination tests, it was decided to use Bentonite N and Sepiolite only, as Bentonite M has unsatisfactory rheological properties and showed lesser cleaning capacity. The tests were carried out on the gray marble facing the left wall of the Chiesa di S. Maria dei Miracoli (Venice), impregnated by soluble salts which XRD identified as aphthalite [$K_3Na(SO_4)_2$] thenardite [Na_2SO_4] and gypsum [$CaSO_4 \cdot 2H_2O$].

Five packs of each clay were applied and removed after spontaneous detachment of the dried mud. Bentonite N was very effective and the wall surface is now clean, with no salt residues. On the pack detachments surfaces, are recrystallized anhydrous Na and Ca salts (Fig. 3).

In Fig. 4 are the results of the conductimetric measurements carried out on the water of extraction of the salts from the packs. They show that Bentonite N and Sepiolite have equivalent desalination capacities, though there is only a minor decrease in the salt concentration from the first to the fifth pack applied to the wall. This must contain large amounts of salt and therefore much more de-salting applications are needed.

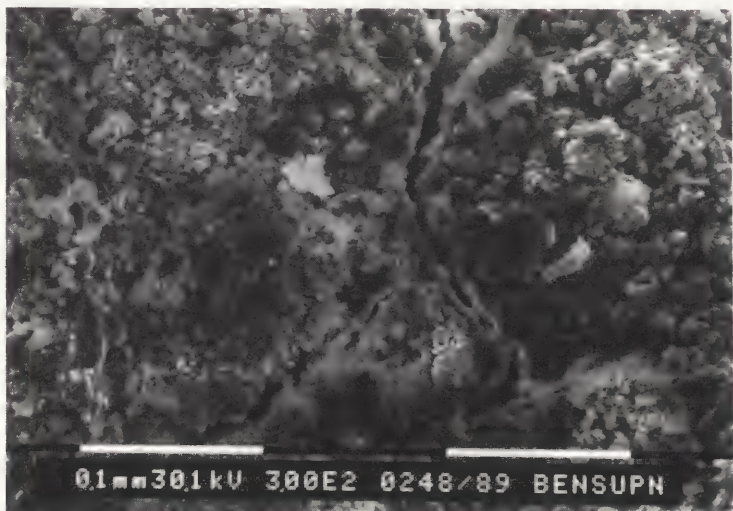


Fig. 3 SEM micrographs as in Figure 2. Microcracks and white salt efflorescences are visible on the surface of detachment of the Bentonite pack.

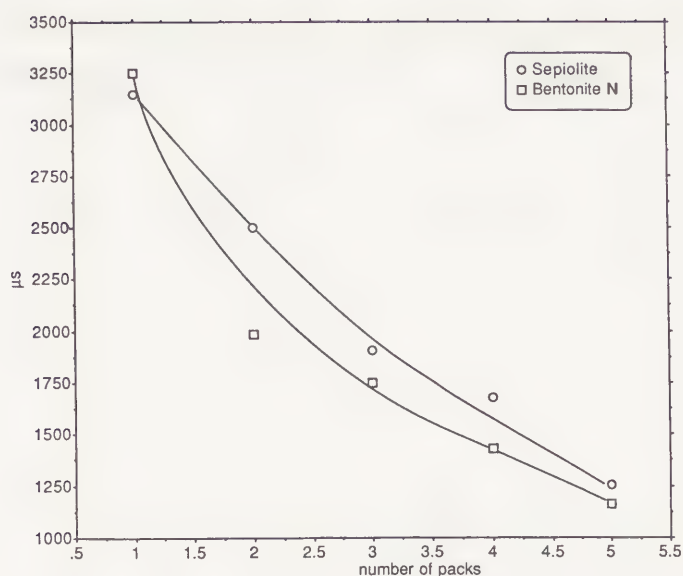


Figure 4 Results of the conductimetric measurements carried out after application of 5 packs of Bentonite N and Sepiolite.

Conclusions

The experiments carried out in this work, though limited to two types of stone and both of them carbonatic, provided evidence that non-activated sodium bentonite has cleaning and desalination properties comparable or superior to sepiolite. Bentonite in its natural state apparently has properties more adequate for these applications than the finer-grained micronized type.

Acknowledgements

The Authors are grateful to ICL, Laviosa, Livorno for providing free samples of Bentonites and to the restorers Antonio Martini and Liliana Zambon for their kind assistance in conducting the cleaning and desalination tests.

References

- 1 - K. Hempel (1968) Notes on the conservation of sculpture, stone, marble and terracotta. In: "Studies in Conservation", 13, n. 1, 35-36.
- 2 - K. Hempel A. Moncrieff (1972) Summary of work on marble conservation at the Victoria and Albert Museum Conservation Department up to August 1971. Proc. Meet. "The Treatment of Stone", R. Rossi-Manaresi and G. Torracca Eds., Bologna, 1972, pp. 167.
- 3 - M. J. Bowley (1975) Desalination of Stone: a case study. Building Research Station, C.P. 46, Garston, 1-9.
- 4 - A. Paleni S.B. Curri (1976) La contaminazione biologica sulla superficie delle opere d'arte. Proc. Int. Symp. "The Conservation of Stone, I°", R. Rossi-Manaresi Ed., Bologna 281-293.
- 5 - L. Lazzarini (1981) La pulitura dei materiali lapidei; metodi industriali e di restauro. Cedam, Padova, 74-77.
- 6 - A. Marconi (1989) Attuali evidenze scientifiche sul rischio derivante dall'uso di fibre minerali e non, naturali e artificiali. Giornale degli Igienisti industriali, 14, 27-43.
- 7 - M.A. Bertolaccini O. Cerquiglini Monteriolo V. Fassina G. Torracca (1975) Study of some gaseous and particulate pollutants in the atmosphere of Venice (1972-73) and their effect on the deterioration of Istrian Stone. ICCROM, Rome, Internal Technical Report.
- 8 - G.P. De Vecchi L. Lazzarini L. Menegazzo Vitturi (1981) Deterioration due to salt efflorescence on interior marble facing of the church of S. Maria de' Miracoli, Venice. Preprints Int. Symp. "The Conservation of Stone, II°", R. Rossi-Manaresi Ed., Bologna 417-443.

ABSTRACT

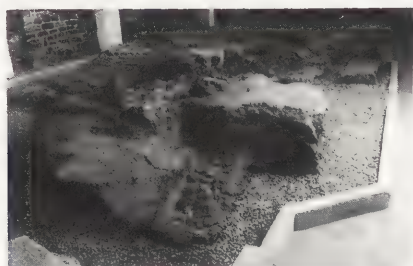
An account of restoration work (1985 - 88) done on medieval relics of stone objects and ceramic pavements in the crypt under the Cathedral of Gniezno will be given. There are relics of old foundations, walls, stoneworks, sculptures, tombs ceramic pavements made of terracotta floor plates. The relics were subjected to scientific examinations with different techniques, including microscopy, chemical analyses and physical tests. The analyses showed that the oldest mortars were made of clay and low-quality gypsum. Different kinds of hard stone were petrographically identified. Porous stones and mortars were consolidated by recrystallization method using barium hydroxide and catalyst to re-cement disintegrated structures. The pavements were lifted and transferred on movable supports. The treatments are considered successful.

KEYWORDS

Cathedral of Gniezno-Poland, ceramic floor replacement, gypsum recrystallization, masonry conservation, mortar consolidation, stone examination.



Cathedral in Gniezno. Medieval stone relics in the crypt.



Medieval stone relics after conservation.

CONSERVATION OF MEDIEVAL STONE RELICS UNDER THE CATHEDRAL OF GNIEZNO, POLAND

Janusz Lehmann
National Museum
Aleje Marcinkowskiego 9
61-745 Poznan,
Poland

Introduction

The Cathedral of Gniezno is one of the most interesting and important historic monuments in Poland. It was founded in 975 by Dąbrówka, daughter of Bohemian Grand Duke Boleslav I, wife of the first historical Duke of Poland Mieczyslaw I, founder of the Polish state, who baptized Polish people in 966. The Cathedral has held the Confession of St. Adalbert since 997; it has been the seat of the Polish primacy since 1000 and was the coronation place of Polish Kings from 1025 to 1305 A.D.

This splendid gothic building developed gradually from a pre-Romanesque temple. By the integration of original parts and rebuilt elements from various periods of different styles it evolved its present form.

At the end of World War II the Cathedral was partly damaged and burnt, and subsequently reconstructed. There were very fruitful archaeological explorations done within the framework of reconstruction. Many interesting architectural and sepulchral relics were discovered, and then under the nave and aisles a big crypt was constructed.

In addition to tombstones, tombs and sepulchral remains (mainly skulls and bones, but also clothes, footwear and adornments) there were stone masonries of different foundations and walls, 3 - 4 layers of ceramic floor plates, fragments of medieval stained glass, sculptures and stoneworks (mostly fragmented), the oldest inscription in Poland on a fragment of stucco tombplate, and many other interesting antiquities.

Since 1985 conservation work has been carried out in order to make the crypt accessible for visitors. Many examinations and some original methods of treatment of stone objects have been applied.

Examinations

In order to record characteristics of stones, mortars and ceramic floor plates, the following examinations were carried out:

- Macroscopic examination (hand lens)
- Microscopic examination (Zeiss-Technival stereomicroscope)
- Chemical tests for resistance to water and acids
- Chemical partial analysis; semi-quantitative determinations of H_2O , Na + K, Ca + Mg, Al + Fe, SiO_2 , pH; solubility in water and in 10% HCl
- Physical tests for density, porosity, specific surface* and heat of wetting.

1. Stones

The relics of the foundations and walls situated in the crypt under the Cathedral are built of irregularly broken, erratically placed blocks and boulders. There are primarily hard and resistant kinds of igneous and metamorphic stones present such as granites, diorites, quartzites and gneisses. Some 19 varieties of hard stone have been petrographically identified. Less than 10% of the stones from foundations and walls represented sedimentary rocks; most are silico-ferrous-calcitic sinters.

2. Mortars

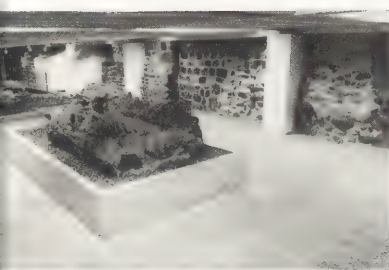
In the relics of the oldest foundations (10-13 centuries A.D.), mostly clay mortar with some lime was used for bedding and joining stones. In walls made in this period gypsum mortars with some calcium and magnesium carbonates were found. The quality of these mortars was poor; some portions were already partly decayed. They were probable made of burnt local lake chalk that contains magnesium. Lime/sand mortars first appeared in walls of the 13th century.

3. Ceramic floor plates

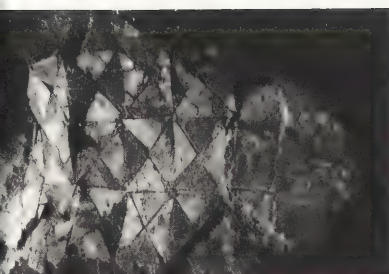
The floor plates were made very skillfully of local clay with a homogenous and smooth ceramic mass. Surfaces are covered with lead glaze which was green, blue, brown, red and yellow in color.



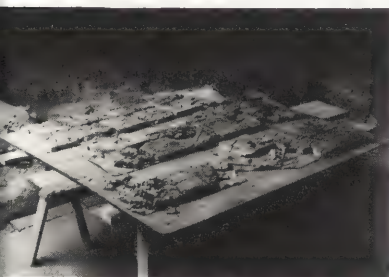
Stone relics before conservation.



Medieval stone relics after conservation.



Relics of early medieval pavements in the crypt under the Cathedral of Gniezno during conservation.



Pavement relics during conservation.

4. Experiments with consolidation of decayed gypsum mortar

The efficacy of the removal of soluble salts by repeated extraction to the moist lignin was checked by means of an electric conductometer. Consolidation of gypsum mortar was tested by applying various concentrations, and with diverse catalysts of recrystallization as urea, glycol, silica, white lead.

*) total internal surface of porous matter (sqm/g).

Conservation

1. Treatment of stone and of mortar

Foundations, walls and tombs were built of various types of stone. Foundations and walls consist of local stone, mainly unevenly broken blocks and boulders of coarsely chipped glacial provenience. Three types of mortars were used: clay/lime, gypsum/lime and sand/lime. The process that was adopted for restoring stone masonry of foundations and walls is as follows:

- The surfaces of stones and joints were cleaned using brushes and sponges moistened with water. The residual stains of mortar and other dirt were eliminated by using paste consisting of bone glue, water, ethylene glycol and sodium versenate. This creamy paste was applied four to five times directly on the surface of stone with a brush. Then gauze was applied and covered with one more layer of paste. After about two days, the paste which formed a skin while drying, was pulled away, thus detaching all residual dirt from the stones.
- Cleaning the joints was done with a hard brush to remove dirt and crusts. Then the joints were carefully washed with de-ionized water with a small added amount of non-caustic detergent, and rinsed many times with water.
- Desalinization of gypsum/lime mortars and porous sorts of stone was done by moistening with a fine spray of distilled water followed by the application of a moist lignin poultice for about two weeks.
- Weak mortar joints and porous stones were consolidated with a solution of barium hydroxide (baryta water) and catalysts.
- Stones and mortars were dried with warm air from a fan (temperature $\sim 100^{\circ}\text{C}$).
- Joints were aesthetically improved by removing excess mortar or by filling in lost mortar.
- Stones were lightly varnished with a diluted (5%) solution of acrylic polymer (Osolan KL of Polish production) in a mixture 1:5 of methanol and ethyl acetate.

2. Conservation of ceramic pavements.

The relics of ancient ceramic pavements were found in subsoil 2,5 - 2,8 m beneath the actual level of the Cathedral's floor. They were fragmented and mostly destroyed when shaft graves were constructed for queens, duchesses and ecclesiastical dignitaries. There were about 5 layers of floor plates of terracotta of various shapes and sizes, partly covered with green, blue, yellow and colorless glazes.

The first consideration in preserving the pavements was to lift particular layers and to preserve the oldest one in situ. The operation for separating ceramic pavements was as follows:

- Each successive layer of ceramic floor was loosened, and then cleaned by using brushes and moist sponges. The revealed surface was divided into areas of 0,3 - 0,5 sqm (suitable to lift as single section) by cutting along straight lines in regard to the decoration, and delimiting selected areas by removing mortar from joints.
- Two layers of strong synthetic fabric were attached to the surface of cleaned pavement by a coating of strong bone glue with 2 - 3% glycerin. When necessary, fresh prepared polyurethane hard foam was poured out on the surface, in order to keep the original curvature of lifted pavement intact.
- Long steel blades were inserted into the clay mortar between ceramic floor plate layers levering sideways, gradually a particular area loosened.
- The removed portion of floor plates was inverted on a flat board, so that surface of pieces were encouraged to lie in one plane. The back was cleaned, as described in point a). Two layers of polyester resin were alternated with glass fabric (lamination). Polyester resin was used to attach a strong synthetic net to the back of lifted pavement; freshly prepared hard polyurethane foam was applied to a thickness of about 4 cm. Before the foam hardened, the surface of the back was leveled and smoothed.

- e) The pavement was reversed, and the facing removed. The polyurethane foam was cut and removed. The bone glue was moistened with hot water, which allowed the synthetic fabric to be removed; patience and prudence are necessary in this operation. The fabric cannot be torn off until the adhesive is sufficiently softened for it to slide over the surface. The process may be facilitated by use of plastic foam sponge soaked with water to swell the glue. It is important to ensure that every trace of glue is removed from the surface.
- f) A detailed examination is necessary to verify that all ceramic floor plates adhere well to their new support. The surfaces are cleaned with organic solvents, and coated lightly with varnish.
- g) The last lower pavement was lifted as described above. Weakened clay mortar underneath was reinforced with 10% solution of acrylic resin Osolan KL in ethyl acetate and methanol (5:1) by deep impregnation, and then the pavement adhered with polyurethane glue Izokol (Polish production).

REFERENCES

- Plenderleith H.J.(1968), 'Problems in the preservation of monuments', The conservation of Cultural Property, UNESCO, Paris 1968.
- Lewin S.Z., Rock E.J.(1976), 'Chemical considerations in the cleaning of stone and masonry', The Conservation of stone, I, Bologna 1976, pp. 343-368.
- Riederer J.(1971), 'Stone preservation in Germany', Conservation of stone, IIC-Conference Preprints, N.Y., IIC London 1971, pp. 125-134.
- Domaslowski W. Lehmann J.,(1972), 'Recherches sur l'affermissement structural des pierres au moyen de resines thermoplastiques', The treatment of stone, Bologna 1972, pp. 255-272.
- Lehmann J. (1976), 'Quelques nouvelles recherches sur le nettoyage et la preservation des sculptures en pierre exposées à l'exterieur', The Conservation of stone I, Bologna 1976, pp. 343-368.
- Lehmann J. (1984), 'Konservierung von steinernen Museumsobjekten' Kolloquium ber Steinkonservierung, Muenster 1984, pp.158-168.

ABSTRACT

Conservation treatment of the gypsum moulding after the bronze sculpture by Vrubel. In the past this sculptural group was a subject of crude conservation intervention. Re-assembling of the multi-figured sculpture was carried out in that way to give a chance to dismantle the group easily.

KEYWORDS

Conservation, damage, gypsum, re-assembling, sculpture, transportation.

THE PROBLEM OF CONSERVATION TREATMENT OF THE UNIQUE GYPSUM SCULPTURE WITH DUE REGARD FOR ITS POSSIBLE REPEATED DISPLACEMENT

Yuri A. Lyubchenko

Grabar Conservation Centre. 60/2, B.Ordynka, Moscow
USSR

Artistic heritage of a great artist knowns no second-rate works: everything he or she created be it a summit within the main creative trend or his/her creation outside the mainstreame of artistic interests sums up the entire previous experience and introduces, at the same time, a new stage. It is an embodiment of the artist's potential and a certain stage of his artistic progress, it is a mistery of art's existance. It is understandable, therefore, why museum workers the world over are working tirelesely to identify all creations of great masters and to incorporate them into their expositions.

In 1929, the State Tretyakov Gallery bought a plaster cast of a group by Vrubel "Robert and the Nuns" presenting a male and three female figures.

An analogous group in bronze is found in one of the mansions in Moscow that formerly belonged to Savva Morozov. Fedor Shekhtel, a well known architect, author of the design for the mansion invited Vrubel to take up interior decoration.

The group represents a scene from Meyerbeer's "Robert le Diable" (libretto by E.Scribe and J.Delavigne) in which Robert is carried away by the evil spirits in the shape of nuns.

It is practically impossible to establish whether the sculpture had been already damaged when the Gallery bought it. One may suggest taht since it was part of the exposition it was in a good state of conservation at that time. Some time later, with the regular shift of the exhibits it was taken to pieces and moved to the storing premises.

In 1986, the four plaster figures accompanied by numerous broken off fragments and smaller pieces arrived at the Grabar Conservation Centre.

The preliminary investigation showed that to be exhibited the figures had been joined together with plaster. This made them a cumbersome and heavy object that could not be moved unless taken to pieces.

Being a complicated task this operation proved beyond the possibility of the Museum's staff. As a result, the sculpture was badly damaged with each of the figures being spalled along the perimetre with broken off fragments in the places where the figures were joined together. The male figure representing Robert lost some of the fingers of the right hand, the left foot and part of the sword. One of the female figures also lost its foot. Parts of the foundation have also been broken off just as the connecting elements of "interwined hands". Judging by the traces the connecting elements ("the bats") were removed in the process of taking the group to pieces. They cracked and some of them were lost.

The existence of an analogous bronze sculpture permitted to conserve the plaster cast in greater detail. Many interesting and unexpected discoveries were made in the process of identification of the groups, careful scrutiny of their surfaces and comparison of the fragments' copies, sizes and photographs.

We have confirmed our previous opinion that the groups were identical according to their main parameters (their sizes, the correspondence between the plastic masses and the greater part of the surface details).

The differences in certain fragments were quite important as they confirmed that the plaster cast was unique.

The fingers of Robert's right hand of the plaster cast proved to be different from the fingers of the bronze sculpture: while the fingers of the plaster cast are elongated and slender, the fingers of the bronze sculpture are thicker with their tips flattened.

Robert's sword is also treated differently. The bronze sword is a rigid and symmetrical copy of a real weapon devoid of any intended deformations, while the plaster sword is undoubtedly the work of an artist with the plastic characteristics and asymmetry peculiar to the entire group. Besides, the sword on the plaster sculpture is turned to the left hand which, probably, suited the composition. On the bronze figure the sword is turned to the right hand, probably, according to the client's wishes.

It looks as if the more fragile elements were damaged when the sculpture was being cast in bronze and were corrected and finished by the same workers which explained considerable differences in the general plastic characteristics. It seems that they finished the bronze surface as well: it is qualitatively different from the plaster surface finished by the author himself.

The comparison of two sculptures testifies that the plaster group was one of the first casts that served the working model for the bronze sculpture.

This makes it especially valuable: the group is the first (author's variant), the exact copy of the original sculpture made in a plastic material that bears no traces of the later corrections and changes.

Its casting indicates that the sculpture was not intended as a museum piece: the figure's foundations were multi-layer rough surfaces with many hollows, brittle edges and wooden supports. The figures were poorly joined together and unstable. As a result some fragments have been lost and the figures have been spalled. Conservation and finishing of the surface were needed to make the plaster cast an exhibition piece. Judging by the state the group reached the Grabar Conservation Centre the missing fragments had been crudely restored and the figures had been joined together in total disregard of the author's surface. Plaster had been used to fill in, the missing details supplied without any regard for analogies. The plaster

used to join the figures together concealed the misjoints caused by poor workmanship. It also covered parts of the original surface.

One of the key problems, the hand of the figure to the left of Robert, was attached in the wrong way (open palm upwards). This was discovered through a careful scrutiny of the hand's surface, the specific features of its modelling and comparison with the bronze cast.

The sculpture's large size and the resultant heavy weight, the composition (the figures joined together to form a ring) and also the numerous minor protruding details of the brittle plaster cast make the sculpture vulnerable. Any attempt to move it without taking it to parts is doomed to failure. It was decided, therefore, to make it collapsible so that it could be moved safely. It has to be disunited into the figures joined together by the original joints without plaster or any other material that would rigidly connect them. It was especially important to make every part stable enough, to determine the exact shape of the joints and to take into consideration the mutual positions of the figures in the group.

Having cleaned the surface and strengthened the figures with polymer impregnation we placed the figures on the specially designed pediment. They were arranged according to the original composition and joined together with the extant original joints.

It was very important to correctly orientate each of the figures according to the horizontal and vertical planes and to temporarily attach them with fastenings. In this way the exact position of the figures was determined. The fact that in any other position the original joints do not fit one another indicates that the original composition has been correctly determined. The position was fixed on the pedestal with marks that corresponded to individual parts of the cast after the entire group had been made more stable and the missing fragments along the perimeter inside and outside and along the joints had been restored.

The outline of the group on the pedestal permits to put the figures on their proper places after the entire composition was taken to pieces to be moved. In this way, the pedestal has become an essential part of the group that ensures its stability.

The group conserved in this way was then taken to pieces and each figure received an individual treatment at specially designed workplace.

The missing fragments - Robert's hand, foot, sword and the foot of one of the female figures, parts of the cloths and fragments of the nuns' intertwined arms - were conserved according to the bronze sculpture and the photographs of the plaster cast on exhibition in the Tretyakov Gallery. It was decided to make many of the protruding fragile elements to be easily detachable when needed with the help of specially devised metal fixings.

Robert's foot is attached to the sculpture placed on the pedestal by a metal clamp; the nun's hand is attached to the arm with the help of pipes fitting one into another. The bats are fixed in different ways that depend on their exact position between the sculptures. Some of them are fastened with a loops or metal rods fitted in the places of the original joints to hooks and recesses strengthened with metal cylinders.

One of the joints, the intertwining of the nuns' arms, is restored with the fragment of plasterpolymer and is easily identifiable on the sculpture. This was done with an eye on the bronze variant though in accordance with the kind of the fragment lost and the type of joints peculiar to the plaster cast. According to the rules such fragments should be easily identified and replaced (if a more exact analogy is found). The Dept. of Sculpture at our Centre has introduced a new practice (to comply with the rules) of making the restored parts of differently coloured plaster. The borders are tinted so that to camouflage the difference but a careful investigation easily brings it out.

Upon conservation treatment, Vrubel's "Robert and Nuns" became a construction of four figures and nine attachable fragments that can easily be taken to pieces and just as easily gathered together on the specially marked podium.

This seems to be the best way out when dealing with a sculpture of a similar size and weight made of plaster.

In the process of detailed investigation of the sculpture that involved documents and reproductions of Vrubel's other works the conservation came to the conclusion that Robert's face reproduces the face of Vrubel with all inevitable transformations that such work involved.

One of the women faces bears resemblance to N. Zabela-Vrubel, the sculptor's future wife and his only and true love. There is nothing amazing in these resemblances: the sculpture was made on the eve of Vrubel's marriage (according to his letters).

In this way the plaster original that has preserved all the original features of the author's design and that is the only of Vrubel's sculptures cast in bronze returned to the museum. It illustrated one more page of this glorious yet tragic fate.

ABSTRACT

BACTERIAL DEGRADATION OF LIMESTONE TREATED WITH POLYMERS

The purpose of the paper is to investigate the effect of lithotrophic and organotrophic bacteria on limestone degradation, treated with polyvinylacetate compositions based on, modified with silicon organic compositions.

Methods have been elaborated for estimating the extent of biodegradation of limestone and polymer compositions. Comparative studies of the kinetics of corrosion processes initiated by various groups of bacteria made it possible to determine the intensity and mechanism of microbiological degradation of the materials under investigation.

KEYWORDS

Polymers, Polyvinylacetate compositions, limestone, biodegradation, bacterial degradation.

Yu.P.Petushkova, A.F.Grishkova
10, Krestyanskaya pl., VNIIR
109172 Moscow,
USSR

Introduction

Polyvinylacetate (PVA) dispersions, along with other polymer materials, are used as binders and glues in the restoration of cultural monuments. Compositions based on PVA with improved properties and enhanced stability against ultraviolet, temperature and moisture effects have been worked out for the purpose of strengthening and glueing museum objects of inorganic materials. In connection with the fact that one of the causes of damage to objects of art made of stone is biological corrosion, it was important to estimate bioreistance of polymer compositions elaborated for the restoration of stone.

The purpose of the paper is to describe an investigation into the bioreistance of films of the following compositions: PVA dispersion, PVA dispersion containing alkoxyloxanes and poly-metalphosphates (PVATPH), as well as PVA dispersions containing alkoxy- and cyclosiloxanes (PVATS). The effect of microorganisms on the degradation of limestone samples, treated with the above three compositions, was investigated along with this. Nitrifying Phase I and II bacteria and *Bacillus mucilaginosus* were used as test cultures, because the greatest danger for the preservation of monuments is posed by lithotrophic and organotrophic bacteria developing not only on the surface, but also in the depth of stone. Bioreistance of polymer materials to these bacteria had not been studied before.

Physico-mechanical testing of samples was conducted in order to determine the extent of polymer and limestone degradation by the bacteria effect. Investigation of structural changes in polymer film was done by the method of repeated infra-red spectra with disrupted full internal reflection. The amount of dissolved silicon in polymer compositions under investigation was determined by the method of spectral atom emission analysis with inductively connected plasm (ICP) by means of the Jobin Iron instrument. Limestone degradation was judged by a change in calcium ions concentration in the medium in the course of microorganisms developing. Quantitative determination of dissolved calcium was done by two methods: trilonometric titration and by atom-emission analysis with inductively connected plasm.

Dynamics of calcium content change in the solution with microorganisms cultivated in the media containing limestone samples, treated with polymer compositions, has been studied. Stone samples without coating were used as a control experiment. Experiment results showed that curves of calcium concentration rise in the medium under the effect of nitrifying bacteria are S-like in shape. Thus, a noticeable extraction of calcium into the solution 5 weeks later after bacteria cultivation had started. The least intensive dissolution of calcium observed from a sample of limestone treated with PVA dispersion was investigated. Kinetics of corrosion processes, caused by organotrophic spore-forming bacteria, turned out to be more complicated. Bacilli development in a saccharose medium caused an intensive extraction of calcium ions at the beginning of the experiment (up to 800 mg/l 10 days after cultivation started). In time, however, the amount of dissolved calcium decreased until it reached values, close to those at the start of the experiment, in 12 weeks. This decrease of calcium can be explained by the formation of calcium organic compounds hard to dissolve. Stone samples, treated with PVATPH composition, proved most resistant to bacteria.

Comparative investigation results of the effect of bacteria on limestone, treated with different compositions, are given in Tables 1 and 2. If dynamics of calcium change in the solution was determined by trilonometric titration, concentration values of calcium and silicon discharged into solution by the end of the experiment were estimated by atom-emission analysis with inductively connected plasm. As shown by the results, the data, obtained by the two methods, are comparable. In so doing, the latter method is more convenient and easy to apply, as it makes possible to detect simultaneously several elements in a small volume of the solution (1-2 cub.cm.).

As can be seen from Table 1, the maximum isolation of calcium into the solution, in the process of cultivating nitrifying bacteria, was observed from limestone samples, treated with PVATS and PVATPH compositions. These coatings, obviously, activate the immobilization of bacterial cells on the stone surface, and at the same time ensure permeability for bacteria and their metabolic products. Silicon organic compounds in the composition of these coatings seem to be the cause of the higher discharge of silicon into the solution. An experiment with the use of polymer films was conducted in order to ascertain a possible participation of microorganisms in this process (Table 3).

As a result of nitrifying bacteria development, calcium isolation into the solution was accompanied by a decrease in the medium pH and sample weight loss. Limestone treated with PVA and PVATS composition manifested a noticeable reduction in strength (Table 1).

Table 1. Effect of Nitrifying Bacteria on Limestone Degradation, Treated with Polymer Compositions

Polymer composition	Con-tion calcium mcg/ml.	Con-tion silicon mcg/ml.	In % less of sample weight		Destruction load, MPa		pH	
			O	K	O	K	O	K
Without treatment	664	7.7	0.6	0.1	0.4	0.4	7.3	7.8
PVA	694	6.3	0.6	0.2	0.3	0.7	5.4	7.7
PVATPH	770	31.5	0.7	0.1	0.5	0.5	5.9	7.8
PVATS	795	46.9	0.7	0.1	0.3	0.4	6.7	7.8

Note to Tables 1 and 2: the amount of calcium and silicon ions was determined by spectral atom-emission analysis method.

O - analysis results of samples infected with bacteria;

K - samples were not infected.

The sign " - " means that the given variant of the experiment was not conducted.

Table 2 Text Results of Limestone Samples with Different Polymer Coatings, Infected with Bacilli

Polymer composition	Con-tion Calcium mcg/ml.	Con-tion silicon, mcg/ml.	% sample weight loss		Destruction load, MPa		pH	
			O	K	O	K	O	K
Without treatment	295	-	0.8	0.9 ^{x/}	0.6	0.5	7.9	8.1
PVA	345	7.7	1.3	0.5 ^{x/}	0.6	0.6	8.0	8.3
PVATPH	-	-	0.3	0.7 ^{x/}	0.3	0.7	8.2	8.0
PVATS	147	46.2	0.7	0.9 ^{x/}	0.5	0.3	8.3	8.2

^{x/} in this variant of the experiment a development of stone natural microflora was observed in the medium.

At the same time the bacilli effect caused some strengthening of these samples compared to control ones, evidently, under the effect of slime formation, characteristic for this bacteria species (Table 2).

Table 3 Bacilli effect on PVATPH film properties

Experiment variant	Physico-mechanical Destructive stress, , MPa	properties of film Lengthening when fractured, , %	Ca ²⁺ concentration in solution mcg/ml
1. Bacteria infected films	12.4	40	1.13
2. Uninfected films	8.5	202	1.36
3. Starting films (dry)	4.6	212	-

Note: In experiment variants 1 and 2 films were placed in a nutrient medium and kept at the temperature of 28°C for 110 days, then taken out of the medium, dried and tested for their physico-mechanical properties.

The testing of PVATPH films for their physico-mechanical properties showed that, under the bacilli effect, fracture lengthening is considerably reduced, and strenght index is slightly increased. Elasticity reduction of films, infected with bacteria, is evidently linked to migration of plasticizer from polymer. A slight rise in strenght index can be accounted for by structural changes under moisture effect, as well as the effect of slime of polysaccharide nature excreted by bacilli.

Determination of silicon concentration showed that bacteria did not intensify its release into a soluble form. Thus, bacilli development on the film surface led to washing-out of plasticizer, in so doing a silicon organic additive in PVATPH composition remained resistant to bacilli for the time of the experiment (110 days).

Method of infra-red spectra, making it possible to estimate processes occurring in the surface layers of films, was used to study the bacterial effect on the structure of polymer itself.

For this purpose sterile films and films infected with bacilli were tested. Both were kept in nutrient agar at the temperature of 28°C for 23 days, then dried, and after that spectra were taken.

The analysis of infra-red spectra of polymer films, which underwent biodegradation, found changes in the intensity of basic adsorption bands, as compared to the control (sterile) sample. A rise in the intensity of the adsorption band of carbonile group ($C=O$) (1720 cm^{-1}), that was observed, shows that oxidation processes of degradation go on in the polymer. At the same time, there was a rise in the intensity of adsorption band in the 1370 cm^{-1} field, linked to deformation fluctuation of methyl group, and in the 1660 cm^{-1} field (valent fluctuations of $C=C$ bonds). A reduction in the quantity of CH_2 -groups (1420 cm^{-1}) in the sample, subjected to biodegradation, shows a development of initial destruction processes in the polymer. A comparative analysis of infra-red adsorption spectra, shows the prevalence of oxidative degradation at the starting stage of biodeterioration.

Conclusion

Thus, it was found, as a result of a complex investigation of bioresistance of different polymer compositions, based on PVA, and limestone, treated with these compositions, that introduction of silicon organic compounds into PVA did not enhance stability of films against biodegradation. The treatment of limestone with those polymers not only did not protect it from bacteria effect, but in some cases even accelerated stone degradation. At present we are conducting an investigation aimed at a further modification of these compositions to enhance their bioresistance.

ABSTRACT

In the case of gypsum-rich surface crusts of weathered calcareous materials exposed to urban atmospheres, pollutants as especially nitrogen oxides exert their action not only on the carbonatic matter of the material, but also on previously formed gypsum aggregates.

In general, solubility of gypsum as well as its dehydration behaviour are strongly influenced by nitrates. Based on this, a hypothesis is presented taking into consideration the possible physico-chemical effects of nitrates forming in the pores of an already corroded calcareous material.

KEYWORDS

Calcareous stone and mortar, air pollution, calcium sulphate, nitrate.

A HYPOTHETICAL CONTRIBUTION TO THE NO_x PROBLEM IN CALCAREOUS STONE

Josef Pühringer
Björnkällvägen 35
S-18362 Stockholm
Sweden

Johannes Weber
Institut für Silikatchemie und Archäometrie
Hochschule für angewandte Kunst
Salzgries 14/1
A-1010 Vienna
Austria

Introduction

1. The action of sulphur dioxide: The effect of sulphur dioxide on the chemical weathering of calcareous stone and mortar is well known and has been studied extensively, (1-3). Gypsum as the most important reaction product can be found to form the major constituent in the so-called black crusts, which themselves represent the classical weathering feature of calcareous material surface protected from direct rainfall. Even where this crust is not developed, gypsum frequently would occur in fissures and pores of the outer zone of the stone.

As to the physico-chemical processes leading to the mechanical decay of gypsum-enriched stone material, however, there still seems to exist some confusion. The frequently stressed pressure of crystallisation/hydration in the course of gypsum-related decay processes is not likely to fit well to what can be observed in practice. As to dehydration (necessary precondition whenever one speaks about hydration pressures) controlled by the ambient climatic parameters, it cannot occur in moderate climates (Fig. 1). Moreover, the frequently observed sequence of a gypsum-rich crust above a zone of advanced decohesion presupposes a mobility of gypsum that does not agree well to its low solubility in pure water.

2. Nitrogen oxides: The role of nitrogen oxides in the deterioration of calcareous stone is not yet cleared. As to calcium nitrates, Livingstone (4) gives a compilation of possible explanations of the fact that those salts seem to occur by far less frequently in weathering crusts than gypsum, despite the notable concentrations of nitrogen oxides in the urban atmosphere.

As stated in (2), for 40 years it has been known that nitrogen oxides can catalyze the processes in the chain of reactions which occur on calcareous materials, such as the reaction with sulphur dioxide in the polluted air to form gypsum or sulphite. Laboratory experiments performed on (polished) calcareous specimens and other materials proved that oxides of nitrogen do have a catalytic effect on the adsorption (chemisorption) rate of sulphur dioxide (5).

Some principal questions about the mode of action of gypsum in and on the surface zone of stone, however, are not answered by the above insights. Furtheron, the exponentially increasing damage rate of calcareous materials in urban environments, noted namely in the post-war time, does not seem to be explained sufficiently.

Taking once more into account that the surface layers of calcareous building materials exposed to an urban atmosphere are not any more calcitic in composition, but to a high amount already converted to gypsum (unless in areas directly exposed to rain or run-off water), one can state that the effect of air pollutants nowadays is exerted on a layer which consists of two-thirds gypsum rather than on a calcareous stone. In view of this, the present paper tries to put up some hypothesis on what could happen to calcium sulphate (dihydrate) when exposed to the action of nitrogen oxides and their products.

The possible action of nitrates on gypsum in stone

1. Generals: The decomposition of calcareous material as cement or micritic matter occurs in several stages: the first one is of chemical nature, converting calcium carbonate into gypsum, causing a first weakening of the binding material; the second stage is physical in which gypsum structures, due to dissolution/recrystallisation or dehydration/hydration, respectively, are altered to finer structures of higher (surface) energy. These structures may swell and shrink in diurnal cycles (dewpoint crossings etc.) under the influence of moisture and heat.

At the surface, processes in a gypsum-water system follow the variations of RH and T in the environment. The system is more or less an open one: eventual dehydration of gypsum to insoluble and soluble anhydrite or to semi-hydrate is governed by external climatic conditions and hence unlikely to occur in moderate climates.

In a more or less filled pore space, the gypsum-water system is a closed one: the equilibrium of the existing salts depends in principle on the vapour pressure of the phases concerned and on the temperature, i.e. on RH and T.

2. Effects on gypsum solubility: Nitrogen oxides as atmospheric pollutants would, even if only to a small extent, form calcium nitrate (tetrahydrate) by reaction with calcareous material. The effect of this calcium nitrate on the gypsum already present in the pores can be as follows:

Nitrate solutions, especially in intermediate concentrations, increase the solubility of gypsum and promote eventual hydration reactions (6). Thus, the above mentioned solution/precipitation cycles are likely to be favoured by the presence of a calcium nitrate solution.

3. Dehydration effects: Due to its saturation moisture of about 55 % RH, calcium nitrate in saturated solution can dehydrate gypsum to anhydrite. The same mechanism has been verified for gypsum in nitric acid (7). At least theoretically, at temperatures as low as ca. 15 °C, gypsum thus can be converted to insoluble anhydrite (see Fig. 1, 2). Such a dehydration will always be associated with an increase in the surface area (due to decreasing particle sizes) and thus with an increase in surface energy, i.e. moisture-related decomposition processes will have a greater effect (8).

It has to be kept in mind, however, that saturation moisture values are only known for relatively large solution surfaces. Small volumes of a solution in pores, where the solution surface corresponds to curved menisci, may shift these values in some way (8).

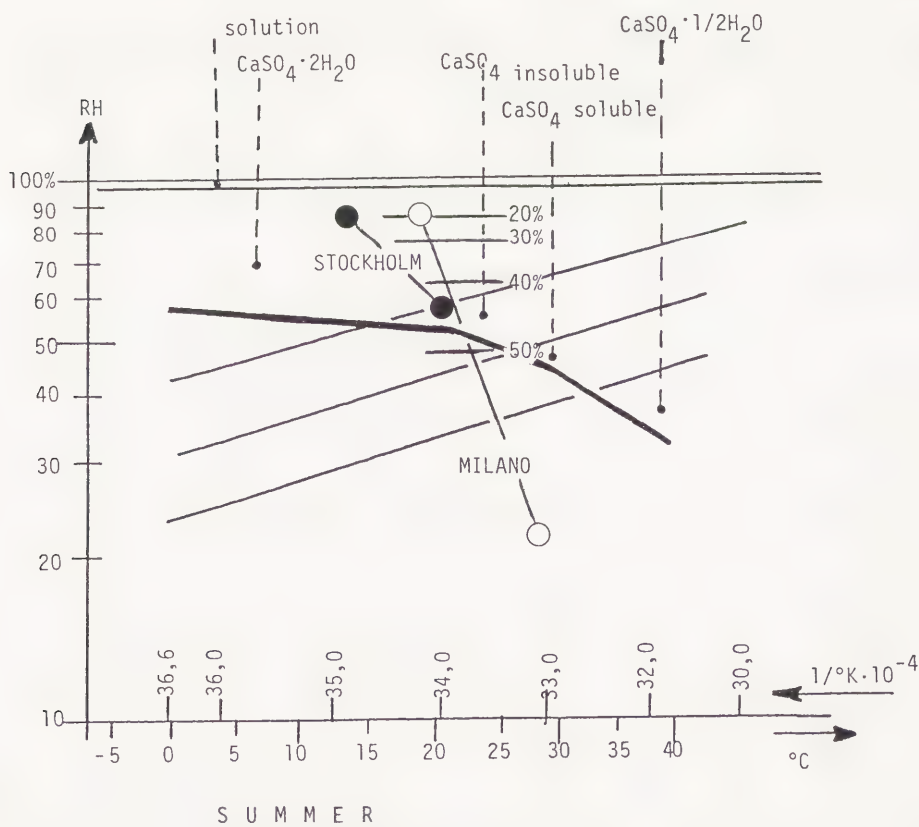


Figure 1: Stability ranges of calcium sulphate phases in the RH/T field, after (7); the fat curved line marks the saturation vapour pressure above a concentrated solution of calcium nitrate, after (12); bars "Stockholm" and "Milano" base on recorded values for summer months of these two cities, (13), (14). It can be seen that above ca. 15 °C calcium nitrate in conc. sol. can cause dehydration of gypsum; it is likely that environmental conditions close to the nitrate line would favour the dehydration reaction to be efficient. - Horizontal lines refer to RH above a solution of nitric acid of the given concentr.

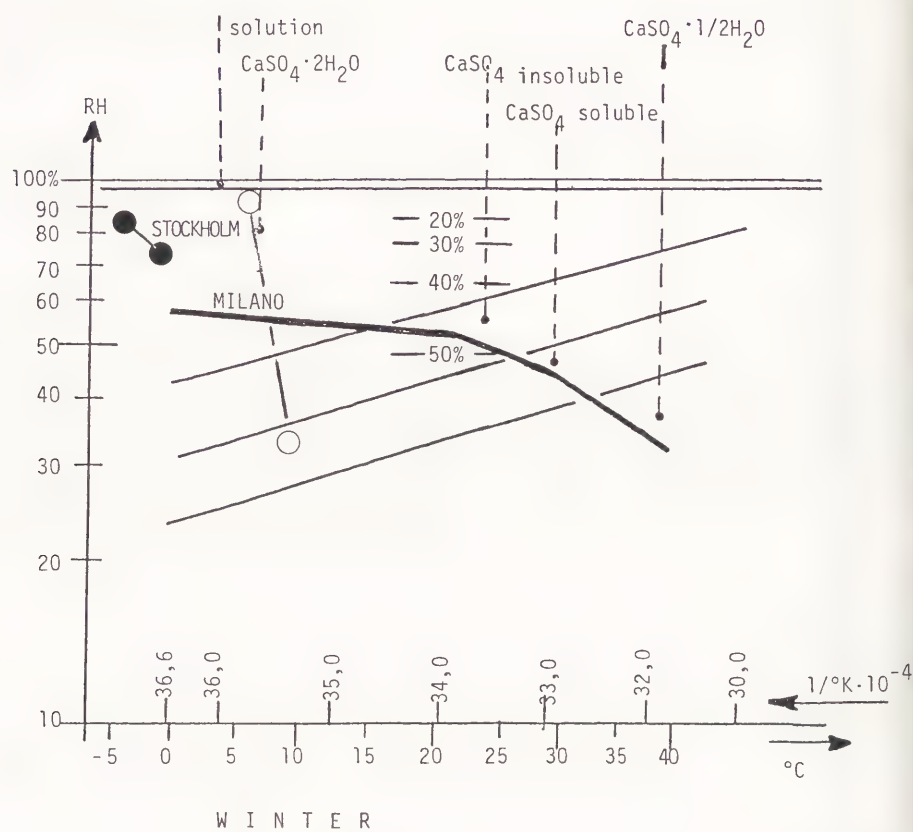


Figure 2: Same as Fig. 1, but with winter values for Stockholm and Milano (13), (14).

Discussion and conclusions

As already mentioned, the presence of calcium nitrate in deteriorated surface zones of monuments and facades can hardly be detected, even in the case of heavy traffic environments. This salt is readily soluble and will therefore wash away by even small amounts of circulating pore water. However, it is mainly the situation of small quantities of water present in the pore space of materials which, in conjunction with dry deposition of pollutants, will produce an aggressive, chemically active solution and allow for the deposition of corrosion substances within the pores. Moreover, the concentration of pollutants in condensed water can be up to 100 % higher than in rain water (9).

This implies that extremely small quantities of water, formed by condensation cycles of high frequency, contain large quantities of aggressive substances; any acid formed under these conditions will be concentrated.

In conjunction with capillary condensation, it will mainly be the smallest pores to be affected by aggressive solutions and the processes induced by them. In a structure of gypsum particles (crystals), which is likely to represent a microporous system, the following may happen:

In the case of gypsum dehydration, possibly induced by calcium nitrates or nitric acid, and when the system is closed to effective water transport, the total volume of the gypsum-water system will increase by 9 % on dehydration, i.e. by the same order of magnitude as in the case of freezing water.

Thus, calcium nitrate as salt or in solution, as well as nitric acid, can cause either refinement of gypsum structures with the consequence of moisture-related swelling/shrinking processes, or "dehydration pressures" by means of gypsum dehydration. This dehydration seems to be in some way irreversible, as "the surface of anhydrite does not acquire the properties of gypsum even after storage in water for 24 hours. The surface of anhydrite is extensively hydrated, but the differences in zeta potential show that there must be large differences in the properties of the materials" (10).

The aggressive effect of nitrogen oxides and nitrates would be most efficient when a RH of 50-60 % stabilises the chemical behaviour of a gypsum-nitrate- water system, as precondition for a long enough contact time between the reagents in a slow process (a few weeks?).

The moisture-related behaviour of a relatively stable gypsum aggregate (which depends on changes in vapour pressure, i.e. changes in RH) is altered in a negative way when affected by nitrates.

On dehydration, dihydrate crystals turn into fine particle structures of cryptocrystalline (amorphous?) anhydrite with an effective surface area that is large with regard to moisture effects: swelling and shrinking as well as dissolution (due to the dispersiveness of fine anhydrite particles) will be much more likely to occur than in the "original" dihydrate structure.

As to the dissolution rate of calcium sulphate, which is little soluble compared to other salts, the solubility-raising effect of nitrate solutions as well as the refinement effect outlined above could yield an explanation of the fact that gypsum crusts above decohesion zones occur in places perfectly protected from rain or run-off water: Cycles of moistening by small quantities of water can be sufficient for solution and transport of calcium sulphate when nitrates are present.

Concerning quartz sandstones with a calcareous binder, conditions in a water-gypsum-quartz system are probably extremely complicated. In (11) observations have been presented pointing to an important influence of salts in solution on the dissolution of quartz and precipitation of silica.

In concentrated gypsum solutions, quartz as well as gypsum have a zeta potential of about -20 mV, whereas that of calcite is ca. +15 mV and that of anhydrite ca. +5 mV (10). Normally, the zeta potential of quartz is about -50 mV.

The fact that anhydrite has not been detected in weathering crusts of calcareous materials is by no means in contradiction to the hypothesis: X-ray techniques would hardly detect the very small amounts of anhydrite (if ever crystalline) supposed to be present in the small pores, and electron microscopy evidence would be limited by the extremely small grain sizes.

Systematic laboratory experiments on ideal mixed systems will be performed in order to prove whether and to what extent the hypotheses outlined above can be verified.

References

1. A. Kieslinger, Zerstörungen an Steinbauten - Ihre Ursache und ihre Abwehr (Leipzig - Wien: Franz Deuticke, 1932), 56-70.
2. G. Amoroso and V. Fassina, Stone Decay and Conservation (Amsterdam: Elsevier, 1983).
3. E.M. Winkler, Stone: Properties, Durability in Man's Environment 2nd edition, (Wien - New York: Springer, 1975), 92-94.
4. R.A. Livingston, "The role of nitrogen oxides in the deterioration of carbonate stone," in Proc. 5th Intern. Congr. on Deterioration and Conservation of Stone, Lausanne, 1985: 509-513.
5. L.G. Johansson, O. Lindquist and R.E. Mangio, "Corrosion of calcareous stones in humid air containing SO₂ and NO₂," Durability of Building Materials 5 (1986): 439-449.
6. J.H. van't Hoff et al., "Gips und Anhydrit," Z. physikal. Chemie 45/3 (1903).
7. E. Heusinger v. Waldegg, Der Gips 2. Aufl., bearb. v. A. Moye (Leipzig: Theod. Thomas, 1906).
8. J. Pühringer, "Möglichkeiten zur Verhinderung von Schäden durch Salze," in Werkstoffwissenschaften und Bausanierung, ed. F.H. Wittmann (2. Internationales Kolloquium, Esslingen 1986): 359-364.
9. J. Weber et al., "Eine Apparatur zur dynamischen Simulation des Einflusses von Luftschadstoffen auf Materialien," Wr. Ber. Naturwiss. Kunst 1 (1984): 12-23.
10. P. Ney, Zeta-Potentiale und Flotierbarkeit von Mineralien (Wien - New York: Springer, 1973).
11. A.W. Magee, P.A. Bull and A.S. Goudie, "Before rock decay: Chemical weathering of constituent grains by salts," in Engineering Geology of Ancient Works, Monuments and Historical Sites, eds. P.G. Marinos and G.C. Koukis (Rotterdam - Brookfield: A.A. Balkema, 1988): 779-786.

12. K. Ulrichs, W. Laue and H.-D. Renovanz, "Salpetersäure und Salpetrige Säure, Stickstoffoxide, Nitrate, Nitrite," in Ullmanns Encyklopädie der technischen Chemie, vol. 20 4. Aufl. (Weinheim - Deerfield Beach - Basel: Verlag Chemie, 1981) 305.

13. N.N., Bygg 1A (Stockholm: Bygg Mästarens Förlag, 1971).

14. G. Baronio, L. Binda and F. Scirocco, "Accelerated aging and models for the progressive chemico-physical deterioration of bricks in the diagnosis of masonry structures," in Werkstoffwissenschaften und Bausanierung, ed. F.H. Wittmann (1. Internationales Kolloquium, Esslingen 1983): 391-395.

Acknowledgements

Economic assistance for this study was given by the Swedish Council of Building Research and the Central Office of National Antiquities.

ABSTRACT

soluble salts can be extracted from porous materials by introducing several surface-active liquids, which act, amongst others, by changing charge conditions at the interface between pore walls and salt solution film.

The formation of whiskers at the surface is considered as the most effective form of salt extraction. It can be achieved by using appropriate techniques which are discussed in the paper.

Also discussed are the mode of operation and eventual risks of several active treatments.

KEYWORDS

salt extraction, surfactants, alkoxysilane

A MODEL FOR SALT EXTRACTION - SOME PRINCIPLES

Josef Pühringer
Björnkällvägen 35
S-18362 Stockholm
Schweden

Johannes Weber*)
Institut für Silikatchemie und Archäometrie
Hochschule für angewandte Kunst
Salzgries 14/1
A-1010 Vienna
Austria

Introduction

Salt damage occurs in the surface layers of materials - direct salt damage usually up to a depth of one or a few millimetres - in interaction between an external environment (temperature T and relative humidity RH) and a porous material acted upon by water-soluble salts in different concentrations.

In the following, RH and T are considered as governing parameters for the actual salt transporting processes. In the case of variations of T, one should refer to partial water pressure rather than to RH.

In principle, salt damage can be prevented in a more or less conventional way by altering RH and T in the environment and on the material surfaces in such a way that the critical conditions for salt migration and conversion are avoided, further by fixing/encapsulating/converting salts so that these cannot be influenced by critical values of T and RH, or by removing, extracting the salts.

As to the extraction of salts from porous materials, the following conventional in-situ methods are available:

- Extraction of salts by means of the poultice method from salt-loaded surface layers where there is no sufficient transfer of liquid from the inside of the material;
- inhibition (or acceleration) of salt and moisture transfer by electro-osmosis.

An alternative method of salt extraction

1. History: In brickwork in the Old Town of Stockholm and in the sandstone crypts of Riddarhomskyrka in Stockholm, long whisker formations can be observed. They had formed in an even climate over a few hundred years and - with the exception of a thin surface layer - had not destroyed the porous substrate.

In conjunction with the impregnation of salt-damaged historic masonry in Finland and Sweden using solvent and catalyst-free alkoxysilanes (both monomers and oligomers), extreme salt precipitation (sodium chloride and/or sodium carbonate) occurred after a few months in the form of whiskers a few centimetres long (1) (because of the presence of salt, the alkoxysilanes polymerised only some months later).

This "negative" effect was then made use of to extract salts in some cellar vaults of brickwork in the Old Town of Stockholm.

First laboratory tests on the extraction method have been presented in (2).

2. Object, transfer mechanisms and methodological requirements: The object of an extraction method is that the salt should "extract itself", i.e. once the efflorescences have initiated they should enable further salt crystallisation.

In view of this, the formation of whiskers appears to be one of the most effective extraction mechanisms. The object of a salt extraction process thus should be to achieve effective whisker formation, if necessary in combination with measures that prevent decomposition of the surface layer of the material in the initial stages of whisker formation.

This extraction process requires the ambient RH to be a little lower than the saturation RH of the respective salt. If RH is too low, evaporation and drying of the salt solution will take place in the material below the surface or in form of a salt crust (3), with the risk that salt deposition, and salt damage will occur, while if RH is too high there is hygroscopic moisture adsorption and dilution of the salt solution; the material surface shall therefore be moist but not wet in order that whisker transfer should occur.

*) Author to whom correspondence should be addressed

Porous materials saturated with salt solution can dry out accompanied by whisker-like efflorescences, which requires some special transfer mechanisms:

- Surface diffusion of salt solution on pore walls, objects' surfaces and whisker surfaces (this effect is known from the drying of salt solutions in glass containers, where the salt formation in the drying zone on the walls of the container is connected to the salt solution in the container through a zone of salt solution film of varying thickness);
- capillary transport within a fine structure of salt crystals coating the pore walls, and in the bunch of porous whisker aggregates.

Under the assumption that there is surface diffusion on whisker surfaces and capillary transfer in the bunch of whiskers, whiskers can, at least in an initial stage, grow at the top (4). The up-lifting of decomposed substrate material on the top of a whisker, as e.g. described in (5), is a surface tensional phenomenon (6); in any case, the whisker top lifts up surface layer particles which had already been sheared off.

Initiation and propagation of whisker formation is also determined by the detailed surface geometry of the material. Owing to surface energy, whisker formation is concentrated to energy maxima, i.e. geometrically to spots, edges or similar sites on convex surfaces.

In principle, the transfer mechanisms which lead to whisker formation of course also hold for the formation of any other kind of efflorescences, like porous unordered particle structures of salts at the material surface/pore opening.

The mobility of liquid films on, primarily, mineral surfaces is partly governed by the electrical charges on the boundary surface between the solid phase and the liquid.

The effect of a liquid transfer on material surfaces due to surface diffusion is governed by vapour pressure (vapour pressure distribution above the surface of the salt solution film). To a certain extent, this might hold also for capillary transport mechanisms.

The object of an extraction method is to convert, in some way, the bulk of liquid/salt bound to the material pores into more or less mobile salt solution films.

Thus, the requirement for a salt extraction method based on whisker formation is that it should modify the vapour pressure (RH) outside the pore opening in the appropriate direction and that it should set up the appropriate electrical charges on material surfaces or of the salt solution film, respectively.

The first requirement is satisfied by a simple moisture physics process. The second requirement can be satisfied by using surface-active preparations.

For geometrical reasons, material transfer requires that the pores should be relatively coarse (transfer pores in the range of 1,5 μm , ca. (7)).

Description of the method

1. Principles: As shown above, the object of the method is to create thin salt solution films, capable of being transported through the pores, on material surfaces, by making use of both vapour pressure and surface-active effects (charge conditions) in the boundary layer between liquids or materials which are in principle incompatible (immiscible).

In order to establish some contact between incompatible liquids in the pore system of a material, mechanical energy is required. Introduction of extraction-active liquids into the pore system containing a salt solution can be achieved by vacuum methods, either by immersion of the object in the salt-extracting liquid under vacuum, or - namely in the case of in-situ treatment - by applying the liquid to the surface of a material placed below a vacuum device like a mat of the type used for finishing concrete floors, or a suction hood like that used for measuring the porosity of concrete.

It should be noted that, when high-grade vacuum is used, the addition of a surface-active preparation may cause water/salt solutions to boil. Boiling may also occur when alkoxysilanes are exposed to an effective vacuum.

These vacuum procedures can be omitted when the extraction-active liquids used have a spreading pressure such that they can be directly distributed over the inner surface even of a moisture-saturated material, or if, through diffusion processes, they can be mixed with salt solutions or water.

The climate outside the pore system can be controlled in the conventional way by many technical methods. A simple way of keeping the RH outside the object below the saturation RH inside the pores is to apply a thin coating which is not in direct contact with the object's surface. Slight heating would cause a sufficient lowering of RH below the coating.

Aqueous solutions of surfactants change not only surface tension conditions but also the saturation moisture content above water and salt solution films.

Thus, if water-soluble-preparations-containing surfactants are used for the extraction of salts, the moisture content of the ambient air must be altered in view of this.

2. Salt transfer: To enable a transport of soluble salts, they must be dissolved in a liquid transfer medium - normally water. This water is brought in to the stone by means of capillary suction, if necessary applying vacuum.

A high efficiency of salt transport to the surface and crystallisation outside the object requires concentrated salt solutions. In principle, it is only concentrated solutions - concentrated at least locally - which can give rise to whisker formation. In practice, however, also subconcentrated solutions will become concentrated in the course of evaporation at the surface.

In case that salt extraction is desired even with small quantities of salt present in the structure, concentrated salt solutions may be obtained by introducing polar liquids that do not dissolve salt, such as alcohols, ketones and similar, eventually diluted with water.

3. Surface modification of materials: As already mentioned, the object of the extraction method is to set up special boundary layers between the pore surfaces of the substrate material, the transferable salt solutions and the extracting liquids, and to create such charge conditions at the respective boundary surfaces that mobilisation of materials, primarily salt solutions, is facilitated or accelerated.

The properties of the material surface can be modified as follows:

- By treating the pore walls with surface-active preparations;
- by altering the surface-active properties of the film of salt solution by applying electrical charges (surfactants);
- by bringing the salt solution film into contact with liquid volumes or liquid films which have special charge conditions on their surfaces.

Active treatment preparations

1. Surface-active preparations: It has been established that alkoxysilanes can extract salts (3,8) (alkyl trialkoxysilanes, tetraalkoxysilanes in monomeric or oligomeric form, presumably for reasons of viscosity).

A partial explanation of the extraction effect of these substances is that they separate water and salt solutions from mineral substrates, presumably as a result of their high spreading power and their low surface tension and viscosity.

However, these preparations also charge material surfaces in a special way even if they do not chemically react with them; thus, they are surface-active preparations with special electrochemical effects.

The salt-extracting effect of alkoxysilanes depends partially on the rapidity of hydrolysis/condensation. This in turn is governed by the existing partial vapour pressure (RH) or the amount of liquid water on pore walls, and on the presence of catalysts/retarders. Salts themselves may act as powerful retarders.

Slow hydrolysis rates seem to increase the effect of the extraction procedure.

Similar to alkoxysilanes, (charge) effects are also caused by cationic surfactants. They also promote whisker formation and initiate salt transport to the material surfaces.

Owing to their different charges, the effect of anionic surfactants is the opposite of that of alkoxysilanes and cationic surfactants (on a substrate).

Generally, the effect of a surfactant depends on the coupling either to a (mostly negatively charged) surface of a substrate or to the surface of a fluid. The reactivity of substrates in relation to different surface-active preparations (such as alkoxysilanes) is varying, especially in the presence of salts.

Surfactants on the surface of fluids may have effects with regard to charges different to those on the surface of a solid substrate or of salt aggregates.

The extraction-active properties of water-soluble surface-active preparations can in part be attributed to their ability to change the vapour pressure above water/salt solutions. They retard or prevent whisker formation.

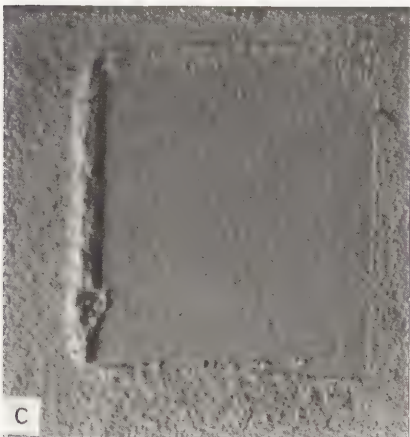
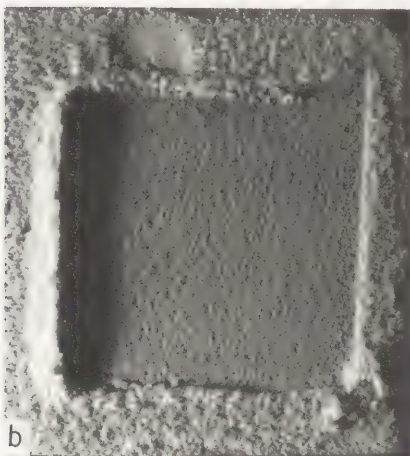
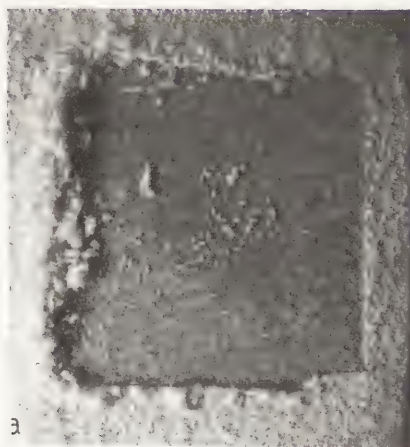


Figure 1: Examples for the extraction of sodium sulphate from Gotland sandstone by application of alkylalkoxysilane (a) and an anionic tenside (b), in comparison to efflorescence without any extraction-active treatment (c). Cubes dimension: 4x4x2 cm; salt solution entered by capillary suction, preparation liquid by immersion under vacuum; drying out for 2 days at 16 °C, 60 % RH. Prior to the photograph, the centres of the surfaces had been mechanically cleaned from salt in order to give a better idea of the thickness of the salt layer.

One disadvantage of all extracting methods is that the solvent/extraction water may distribute salts and moisture towards the interior of the material: this can be avoided applying an apolar medium that does not dissolve salts, such as alcohol or water/alcohol mixtures, prior to the suction by water. The liquid front will block redistribution of salts and moisture through water.

The change of charge conditions on surfaces due to the action of surface-active preparations is also manifested in the fine structure of the salt aggregates formed at the surface. As had been stated previously (9) these structures change in response to fluctuations and changes in vapour pressure.

Solutions containing anionic surfactants dry rapidly, those containing cationic surfactants more slowly. Certain surface-active preparations thus influence the dynamics of salt structure and especially whisker formation.

2. Indirectly active preparations: Naturally, hydrophobic and chemically inert liquids which displace salt solutions, such as many non-polar solvents and similar substances, e.g. naphtha, are also regarded as extraction active liquids. (They can also be used in combination with alkoxysilanes, e.g.)

Solvents which are mixable with water but cannot dissolve salts (as alcohols formed by the hydrolysis of silanes, e.g.) can, under special circumstances, be accounted for as indirectly extraction-active preparations which can change the vapour pressure and RH in and above films and volumes of salt solutions. They change the salt concentration by extracting water from salt solutions.

Of course also water itself acts as a salt-extracting preparation (even water released in the course of the condensation of silanes).

Extraction-active preparations may promote the dissolution of aggregates of solid salt particles in water.

It is possible to combine surface-active preparations with indirectly extraction-active ones. Preparations which are indirectly extraction-active can be vehicles for surface-active preparations such as alcohol-soluble or oil-soluble surfactants.

3. Effects, interactions, material combinations, compatibility: The extraction effect differs between various salts/salt mixtures, for thermodynamical reasons (saturation vapour pressure, critical concentrations, etc.). Preliminary laboratory tests showed that hydrate salts can be mobilised and extracted easier than anhydrides (sodium sulphate better than sodium chloride, e.g.), presumably due to differences in the crystal structures.

When, in the case of sodium sulphate, the growth of hydrate whiskers stops, dehydration can be observed on their top, due to the ambient climatic conditions.

Special reactions can occur between water-soluble salts and surface-active water-soluble preparations. It is not possible to give any general information regarding the effects of these reactions or the conditions governing them; precipitation processes which may occur as a result of these reactions can be used to separate salts from solutions or from other materials. The effect of a given surface-active additive depends largely on the pH of solutions and substrates (and even on T).

Certain interaction effects between substrate materials and surfactants are known from flotation technology (10). Certain interaction effects between salts in solutions and water soluble surfactants are known from, e.g., separation techniques for the production of industrial salts.

There is no general information concerning eventual synergistic effects between the properties of substrates and different salts in relation to the kinetics of whisker formation. Among the most dominating parameters of an extraction procedure are the physico-chemical properties of the substrate, such as pore volume, pore geometry, chemical composition and reactivity. In certain cases, also the mechanical strength and the state of degradation can be decisive.

4. Remarks on applications: The actual process of applying extraction-active substances can, by purely physical means, displace concentrated salt solutions from the pore openings.

If extraction of salts is to be carried out in a number of steps, changes in the substrate material and salt solutions which may have been caused by previous extraction steps must be taken into consideration.

The consequences of the method - advantages and drawbacks

Degradation of a material by water soluble salts occurs largely as a result of the swelling of fine salt particles when these are wetted.

Salt extraction treatment using aqueous preparations can entail certain risks. These risks must, however, be weighed against a future and perhaps accelerated degradation process.

In case of risks of material degradation, the use of non-polar preparations for the extraction of salts is, if possible, to be preferred.

Risks can be reduced by using appropriate surfactants which can influence the formation of structures and the forces arising in the initial state of whisker growth in a favourable way.

It should be the aim of the extraction treatment to prevent salt solution films from drying out during the extraction in order to avoid the degradation of a substrate by (repeated) wetting of salt structures consisting of fine particles.

In the very first stages of whisker formation, material degradation to a limited extent may occur around and just inside the pore openings. This risk can be avoided by applying a sacrificial layer, e.g. some kind of conventional poultice or a sheet of paper or cloth, etc.

Salts extracted by this method can be removed without any major mechanical damage to a material which may already have been damaged by salt, for instance by careful brushing, blowing or suction using air, or by careful rinsing with polar or nonpolar liquids which neither dissolve the salts nor cause swelling.

The field of application of the salt extraction method described above is confined to the surface layers of materials.

The method may be used as a complement to an electroosmosis process in the initial stages, maybe to enhance the effect of electrodes mounted on the surface.

The method has the advantage that the results of extraction can be observed directly (without analysis of the contents of poultices). The results of extraction also indicate the distribution of salts over the surface; as a result, measures to be taken after an initial treatment stage can be concentrated or omitted.

Examples

The salt extraction method outlined above has, on a prototype scale, been used to extract salts from medieval masonry in the Old Town of Stockholm.

Silicic acid esters free from solvents and catalysts have extracted salts after up to two-three months, i.e. before the ester had definitely polymerised.

Results of laboratory experiments are illustrated in Fig. 1-4.

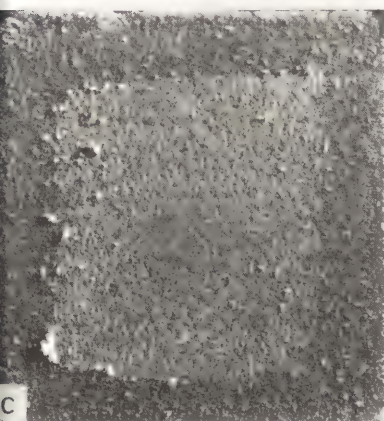
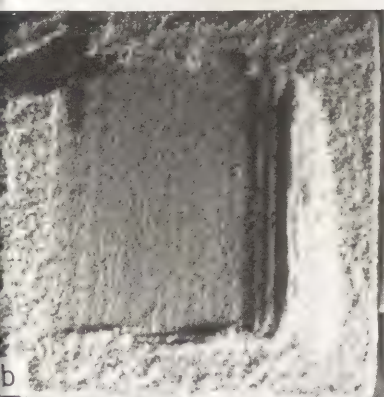
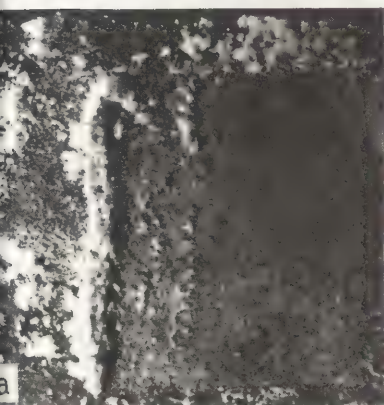


Figure 2: Examples for the extraction of sodium chloride from Gotland sandstone by application of alkylalkoxysilane (a) and an anionic tenside (b), in comparison with efflorescence without any extraction-active treatment (c). For procedure, see Figure 1, despite the time for drying-out of 5 days.

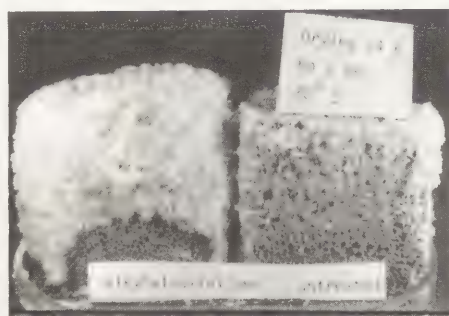


Figure 3: Extraction of sodium sulphate from light-weight concrete by application of alkylalkoxysilane. Procedure as described in Figure 1. Drying out at 20 °C, 60 % RH for 24 h. Tops of whiskers decomposed to anhydrate.

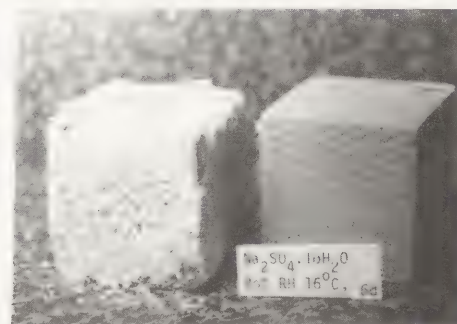


Figure 4: Extraction of sodium sulphate from Gotland sandstone by application of silicic ester. Procedure as in other examples. Drying out at 16 °C, 80 % RH for 6 days. Whiskers are of salt hydrate.

References

1. Th. Perander, Tiiliki vien rapautuminen soumenlinnassa tutkimusraportti, osa III, Valtionillinen Tutkimuskeskus Betoni, ja silikaattekniikan laboratorio (1983).
2. J. Pühringer and Th. Perander, "Extraction of salt from materials of coarse porosity," in Proc. 5th Intern. Congr. on Deterioration and Conservation of Stone, Lausanne, 1985: 251-254.
3. A. Arnold and A. Kueng, "Crystallization and habits of salt efflorescences on walls I - Methods of investigations and habits," in Proc. 5th Intern. Congr. on Deterioration and Conservation of Stone, Lausanne, 1985: 255-267.
4. C.B. Nielsen, "How to characterize pore structures of porous building materials using digital imaging analysis of planner sections," Information Technical University of Denmark, Building Materials Laboratory, October 1989.
5. K. Zehnder and A. Arnold, "New experiments on salt crystallization," in: Proc. 6th Intern. Congr. on Deterioration and Conservation of Stone, Torun, 1988: 320-329.
6. C.W. Correns, "Über die Erklärung der sogenannten Kristallisationskraft," Sitzungsbericht Preuss. Akad. Wiss. 1926: 81-88.
7. R. Snethlage, Steinkonservierung 1979 - 1983, Arbeitshefte des Bayerischen Landesamtes für Denkmalpflege, H. 22 (München, 1984).
8. S.M. Bradley and S.B. Hanna, "The effect of soluble salt movements on the conservation of an egyptian limestone standing figure," in Case Studies in the Conservation of Stone and Wall Paintings, eds. N.S. Brommelle and P. Smith (Preprints of the IIC-Congress, Bologna, 1986): 57-61.
9. J. Pühringer, "Möglichkeiten zur Verhinderung von Schäden durch Salze," in Werkstoffwissenschaften und Bausanierung, ed. F.H. Wittmann (2. Internationales Kolloquium, Esslingen 1986):359-364.
10. P. Ney, Zeta-Potentiale und Flotierbarkeit von Mineralien (Wien - New York: Springer, 1973).

Acknowledgements

Economic assistance for this study was given by the Swedish Council for Building Research and the Central Office of National Antiquities.

ABSTRACT

Most theories concerning the deterioration of porous building materials by the action of salts are based on the assumption of pressures exerted by crystallising and, moreover, hydrating salts. Salt crystallisation tests which exist in various standardised forms mostly base on the "hydration pressure", building up by cycles of soaking with salt solution followed by drying and heating and so on.

However, theoretical considerations as well as simple laboratory experiments lead to the conclusion that hydration of salt anhydrides, namely by action of concentrated solutions, is a process unlikely to occur in the course of laboratory tests. On the other hand, the formation of anhydrides from hydrates always proves to result in very fine-grained, even amorphous aggregates. Their high specific surface and microporosity makes them susceptible to thermohygric dilatation and structural alterations induced by alterations in RH and T. Hydration of such anhydrate aggregates, however, will be very limited.

Based on the above considerations, alternative test cycles are discussed and examples presented.

KEYWORDS

Porous materials, salt decay, salt crystallisation test, salt hydration.

SALT ACTION AND MATERIAL TESTING

Josef Pühringer
Björnkällvägen 35
S-18362 Stockholm
Sweden

Johannes Weber *)
Institut für Silikatchemie und Archäometrie
Hochschule für angewandte Kunst
Salzgries 14/1
A-1010 Vienna
Austria

Introduction

Over the years, a number of theories regarding the degradation of materials by the action of soluble salts have been formulated on the basis of thermodynamical considerations (1-5). It has not been possible to verify these theories by experiments or tests, since the large forces postulated by them seem likely to occur only in micropore or gel-like systems.

Even the "hydration pressure" in connection with the formation of an hydrated salt crystal, presupposing in some way an inward diffusion of water molecules into an ideal (anhydrate) crystal and blocking displacement of a solution, can probably occur only on a geological time scale. (The crystallisation of an hydrate salt out of the solution, the formation of a solid body and the incorporation of water molecules into the crystal lattice always means a decrease in the total volume of the whole system salt/water (with the exception of ice and calcium chloride)).

In practice, salt degradation is associated with transport phenomena corresponding to alterations/increases in concentration, which, in turn, necessitates reasonably coarse transport pores.

Degradation of a porous material by the behaviour of the salt-water system in transport pores is an effect of the mode of action of fine salt particles, mainly under the influence of repeated variations in humidity (vapour pressure) and/or temperature (6).

These repeated processes may occur in the following manner:

- Fluctuations of RH and T in the environment;
- imbalances of the menisci in capillaries due to drying and wetting, in conjunction with capillary transport.

In principle, degradation by the action of salts can occur also when only anhydrate salts are present. Sodium chloride, which above the freezing temperature of water does not form any hydrate, is known to damage brick and stone (7). In the major part of the cases, however, material deterioration due to salts can be attributed to the action of hydrate/ anhydrate salts (8).

Conventional salt crystallisation tests

1 Phase equilibria in the system salt-water: From the thermodynamic point of view, phase equilibrium in a salt- water system depends on only three parameters, namely concentration c of the salt in the solution, absolute temperature T and the partial pressure p of water vapour (alternatively RH and temperature).

The particle size in a salt structure depends on vapour pressure conditions implied to the system.

There is no linearity in any of the ratios between the above parameters. In principle, it is not possible to accelerate a certain process in direct proportion to some other process by increasing in some way the value of a single parameter such as temperature or concentration.

To this must be added the fact that there is a mutual relationship between diffusion and reactions (hydration/dehydration) in processes that occur in physically or chemically unstable salt-water systems, i.e. reactions like the above ones are to be considered as diffusion- controlled.

2. Salt crystallisation tests: In a conventional salt crystallisation test, a porous test specimen is subjected to repeated cycles comprising absorption of a concentrated salt solution, drying and heating at different rates and intensities (9)-(12).

*) Author to whom correspondence should be addressed

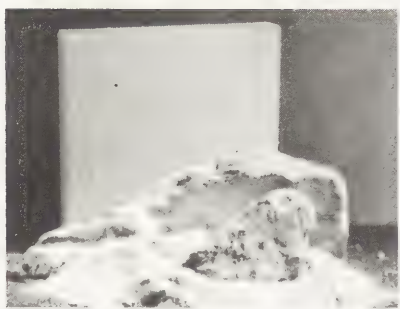


Figure 1: Total break-down of a hard sandstone ("Hopansdan Stone") after only 7 wetting/drying cycles with Na_2SO_4 -conc. sol. Heating was performed by means of microwaves (5 min. of capillary suction - 5 min. of microwave heating).

The number of cycles necessary to achieve material failure is considered to provide a more or less general criterion of the resistance against the attack of various types of salt. Principally, the object of such a test is to break down the test material as quickly as possible. Cycles are formally related to wetting (i.e. hydration) but actually always to intensive heating. (In fact, when using electromagnetic microwaves, seven sodium sulphate cycles of approx. 20 min each can cause severe degradation of a relatively hard sandstone; see Fig. 1).

In such a heat-related cycle, different thermal expansion coefficients of substrate and salt, respectively, can be accentuated. Further, using solutions of salt at a concentration of about 30 % by vol., theoretically approx. 85 % of the pore volume will be filled after only 5 cycles (!). In practice, salts may separate from solutions, the solution may become diluted; the concentration of the solution decreases during its transport.

The results of the conventional tests have been interpreted as a proof that a porous material can be destroyed by a number of hydration/dehydration processes.

In fact, the salt crystallisation test is a proof of the opposite, as will be shown below.

Salt structures formed in accelerated salt degradation processes

In the course of a salt crystallisation test, a porous material is saturated with a concentrated salt solution. This salt solution then is evaporated, the crystallised salt eventually dehydrated.

The salt particles formed in this way may be crystalline such as it is the case with sodium chloride, e.g. However, they may also be amorphous or at least cryptocrystalline, which seems to be the case when anhydrate salts are formed from the respective hydrates - this transformation is likely to occur as pseudomorphs after the initial crystal, especially in the case of relatively rapid dehydration rates.

In any case, formation of salt anhydrides by dehydration of previous existing hydrates always results in very small particles. When this particle system then is brought into contact with a concentrated solution (within the stability range of the hydrated phase), no or only very incomplete hydration reactions can be observed (13). In a suspension of such anhydrate particles in a concentrated salt solution, no heat of hydration reaction can be detected. That means, that a mixture of anhydrate salt particles and saturated solution can coexist metastably.

No hydration and hence no hydration pressures occur in such cases.

When brought into contact with the concentrated solution, "amorphous" particles of salt anhydrides (e.g. sodium sulphate) show crystalline aspects (birefracton can be noticed with crossed polarisers) for a very short time. No explanation of this phenomenon can be advanced as yet. Also, no explanation can for the time being be given for the appearance of vapour "bubbles" followed by their dissolution in some salt formation processes (thermodynamic imbalances?).

The formation of salt anhydrides occurs, as in the case of gypsum, as a dissolution-precipitation reaction (14); the anhydrate first gets dissolved in (salt) water and then eventually precipitates as hydrate crystals. Hydration thus comprises two partial processes.

Repeated addition of a concentrated solution and subsequent formation of salt anhydrate generally causes a refinement of particles or their aggregates. The specific surface increases correspondingly.

These ideal processes can be established and may be visualised for example by a technique using an optical microscope with crossed nicols (polarized light) and adapted with a video recorder and video display.

2. Forces acting in salt crystallisation tests: Apart from thermal expansion (15,16), volumetric changes in aggregates of fine salt particles of large surface area are due only to moisture-related swelling and shrinkage. This hygric expansion would reach its maximum in the case of the presence of a concentrated solution; in subconcentrated solutions there would occur some (limited) hydration accompanied by a partial expansion in volume which would increase the diffusion resistance of the aggregate's surface and prevent it from further refinement.

When porous materials are affected by the action of salt hydrates in equilibrium with subconcentrated solutions, water or water vapour, these hydrates should occur only as thin but tight salt films on the walls of pores.

The reason why sodium chloride salt does not degrade materials in conventional salt crystallisation tests is that, above 0 °C ca., this salt only crystallises as anhydrate with relatively small specific surface - the



Figure 2a: Crystals of sodium chloride dihydrate, stable below 0 °C ca.; magnification 100 x.

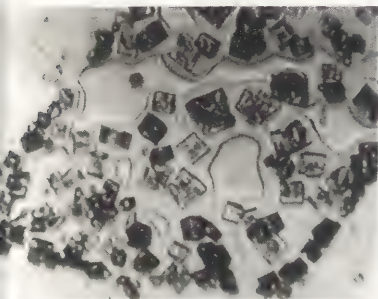


Figure 2b: Small crystals of sodium chloride anhydrate, formed by dehydration from the dihydrate in the course of slight heating above 0 °C; magnification 100 x.

effect of the formation of small anhydrate aggregates, however, can be observed when crystals of sodium chloride dihydrate (stable below about 0 °C) are thawed above 0 °C where they are subjected to dehydration (see Fig. 2a,b). In fact, it is possible to bring about effective degradation of materials treated with sodium chloride when using temperature cycles around 0 °C. On heating, the salt would decompose to small particles of its anhydrate.

Another way to produce small effective particles of anhydrate salts directly from the solution would be to dry out the sample at extremely low vapour pressures (under vacuum or at very low RH).

3. Summary: The effect of salt hydrates on porous materials is generally due to the moisture-related behaviour of thin cement-like films or volumes of anhydrate particles, combined with the effect of partial hydration/dehydration (but not crystallisation) processes.

An outline of an alternative salt crystallisation test

1. Object: The object of a test is to establish the real properties and behaviour of a material, not to satisfy or fail to satisfy established criteria which have varying degrees of relevance.

The decisive material property to be tested is durability, either the initial or the remaining service life with regard to a special stress, assessed in relation to a certain aspect.

The test shall be an aid in checking and improving material properties. Its further object is to determine material properties by means of a test method which simulates real conditions.

In general, a merely accelerated deterioration by means of an accelerated test program can be achieved for many materials. However, as for the example shown in Fig. 1, where microwave heating had been used for drying, it soon becomes impossible to interpret a test result in the correct way (was deterioration of this sample due to salt crystallisation or rather to excessive heating?).

The aim of an accelerated test method should possibly be to increase not the amplitude of the respective events but rather their frequency. An uniform loading cycle of high frequency and a uniform and relatively low loading amplitude does not preclude acceleration of a degradation process.

2. Proposed test method for stress induced by salt (frost/salt): As stated before, degradation of a porous material by water-soluble salts is highly dependent on the moisture-related behaviour of - mostly amorphous to cryptocrystalline - salt particles and their aggregates. Their behaviour is principally governed by vapour pressure and, naturally, by temperature (in practice, it is indirectly governed by RH and T). Hence, degradation of materials by the action of salts occurs due to variations in vapour pressure and temperature (RH and temperature), mostly in the form of cyclic processes (dew point crossing, crossing of critical RH/T values, drying/wetting of menisci in capillaries).

The object of accelerated testing methods should therefore be to increase the frequency of these water vapour fluctuations, in principle by increasing the rate of drying; presumably, it is impossible to increase the rate of wetting appreciably.

This variation in vapour pressure, i.e. in the water content of the ambient air, can in practice be brought about by two simple methods:

- Drying under vacuum;
- drying through convection, possibly accompanied by increased air velocity and warming and drying of the air/gas used (17)

Drying under the above conditions will avoid largely any stress in the surface layer of the material to be tested due to different thermal expansion coefficients of the substrate material and the salt. Further, it will lower the vapour pressure within a whole surface layer rather than cause a moisture reduction only at the very surface.

When drying under vacuum it must be noted that evaporation of water from small test specimens lowers their surface temperature and changes the conditions governing salt transformations; heating may be required to counter-balance this effect.

This phenomenon gives also the unique opportunity to conduct salt/frost tests with high "load frequency". Test samples may get frozen due to the loss of heat by evaporation (at suitable relatively small dimensions of wet samples).

In both of the above cases, wetting can be brought about by the following means: water vapour-saturated air, air containing water or salt solution in aerosol form, direct wetting with low amounts of liquid water,

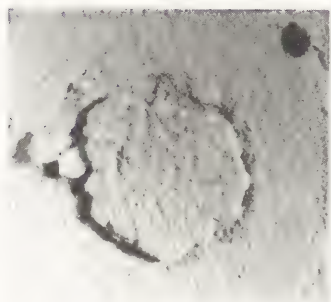


Figure 3: Sample surface of Gotland sandstone after 14 wetting/drying cycles with conc. sol. of sodium sulphate.

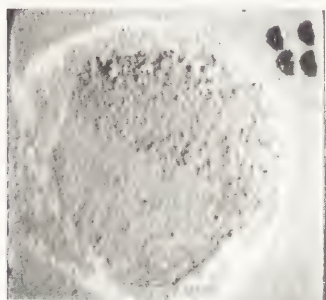


Figure 4a: Gotland sandstone after 4 wetting/drying cycles with conc. sol. of sodium sulphate. The circular shape of the deteriorated zone corresponds to the zone wetted by the droplets.

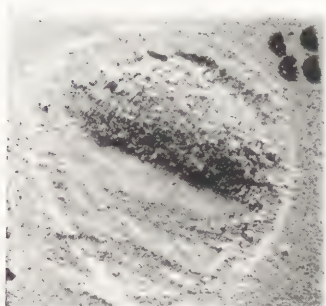


Figure 4b: Same sample as Fig. 4a; after completing cycles with sodium sulphate solution, 4 wetting/drying cycles with water were performed, deterioration was going ahead.



Figure 5: Gotland sandstone after 6 wetting/drying cycles with conc. sol. of sodium chloride, followed by 24 cycles with water. Deterioration follows the boundary of the wetted zone.

The results of these simple tests can be summarised as follows:

No	Material	Salt	Wetting (15min/cycle) No of cycles (sol.)	(H ₂ O)	Drying min/cycle	Deterior. at cycle No.	Fig. No.	total eff. testing time (h)	
1	Gotland	Na ₂ SO ₄	14		30	14	3	11	*)
2			4	(4)	30	4	4	3	**)
3		NaCl	6	24	60	30	5	24	
4			12	4	60	16	6	20	
5	l.w.concr.	Na ₂ SO ₄	7		30	7	7	6	

Remarks: *) Solution penetrated well into sample; damage appears as scaling

**) Solution did not penetrate very well into sample; damage visible already after the 4th cycle of wetting with sat. sol., appears as crumbling

Table 1: Preliminary labor experiments: alternative test cycles on Gotland sandstone and light-weight concrete, using sodium sulphate and sodium chloride, respectively.

5.1. Interpretations: Deterioration of test samples in the course of changing water vapour pressure is not likely to be due to hydration pressures, as also in the case of sodium chloride surface degradation could be achieved.

It could be seen from the test results, that the deteriorating effect of salt seem to depend in some way on the concentration of the solution used. This may have the following reason:

Concentrated solutions do not dissolve the surface of a salt particle. The particle size, the active area of the particle structure, and the pore volume in a porous salt aggregate are changed to a smaller extent on wetting with concentrated solutions than with water.

For the same reason, small amounts of water (cycles of condensation) which do not dissolve the salt structure to a greater extent, have a stronger effect than large amounts of water (of precipitation, capillary transport).

When starting cycles with pure water-wetting in the course of the test, there must be a lowest critical salt content introduced by previous cycles of wetting with salt solution.

The vacuum chamber used in the desiccation cycle of the test had a global shape with a diameter of 35 cm. The vacuum pump had a capacity of water evaporation at a rate of approx. 2-3 g water/h.

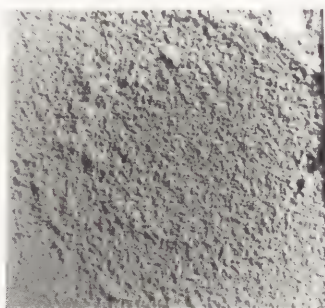


Figure 6: Gotland sandstone after 12 wetting/drying cycles with conc. sol. of sodium chloride, followed by 4 cycles with water. Deterioration is more pronounced than in the Fig. 5 example.

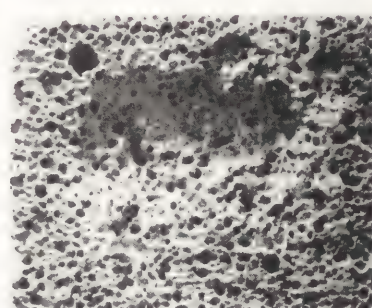


Figure 7: Light-weight concrete after 7 wetting/drying cycles with conc. sol. of sodium sulphate.

References

1. C.W. Correns and W. Steinborn, "Experimente zur Messung und Erklärung der sogenannten Kristallisationskraft," Z. Krist. 101 (1939): 117-133.
2. H. Mortensen, "Die 'Salzsprengung' und ihre Bedeutung für die regional-klimatische Gliederung der Wüsten," Petermann's Geogr. Mitt. 79 (1933): 130-135.
3. J. Pühringer, "Hydrate salts and degradation of materials" in Proc. 5th Intern. Congr. on Deterioration and Conservation of Stone, Lausanne, 1985: 231-239.
4. B. Fitzner and R. Snethlage, "Über Zusammenhänge zwischen Salzkristallisation und Porenradialverteilung," GP Newsletters 3 (1982): 13-24.
5. K. Kraus, "Verwitterung von Naturwerksteinen," Bautenschutz und Bausanierung 11/5 (1988): 143-149.
6. J. Pühringer, "Salzwanderung und Verwitterung durch Salze" in Werkstoffwissenschaften und Bausanierung, 2. Intern. Kolloquium, Esslingen, 1983, ed. F.H. Wittmann: 361-366.
7. E.S. Larsen, "Mursalte, kvalitativ og kvantitativ undersøgelser av salte i teglsten fra middelalderkirker" eksamensprojekt 1987, teknisk rapport 181/88 (Technical University of Denmark, Building materials laboratory).
8. L. Binda, G. Baronio and A.E. Charola, "Deterioration of porous materials due to salt crystallization under different thermohygrometric conditions. I. Brick" in Proc. 5th Intern. Congr. on Deterioration and Conservation of Stone, Lausanne, 1985: 279-288.
9. Building Research Establishment, The Selection of Natural Building Stones, BRE Digest 269 (London: H.M. Stationery Office, 1983).
10. DIN 52 111, Prüfung von Naturstein. Kristallisationsversuch mit Natriumsulfat, Ausgabe Dez. 1976.
11. ASTM C 88 - 76, Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate, Issue Sept. 1976.
12. K. Niesel and P. Schimmelwitz, Zur quantitativen Kennzeichnung des Verwitterungsverhaltens von Naturwerksteinen anhand ihrer Gefügemerkmale, BAM Forschungsbericht 86 (Berlin: Bundesanstalt für Materialprüfung, 1982), 100.
13. J. Weber and A.E. Charola, "Some observations on the hydration/ dehydration of sodium sulphate" (Work in Progress).
14. R. Snethlage, D. Hoffmann and D. Knöfel, "Simulation der Verwitterung von Naturstein, Teil 2: Physikalisch-chemische Verwitterungsreaktionen," in Werkstoffwissenschaften und Bausanierung, 2. Internat. Kolloquium, Esslingen 1986, ed. F.H. Wittmann: 11-17.
15. W. Dreyer, "Materialverhalten anisotroper Festkörper," Applied Mineralogy 7 (1974).
16. C. B. Nielsen, "Termisk deformation og svind af saldholdige teglsten," eksamensprojekt 1987, teknisk rapport 182/99 (Technical University of Denmark, Building materials laboratory).
17. L. Berntsson et al., "Drying techniques" in Proc. 5th Internat. Congr. on Deterioration and Conservation of Stone, Lausanne, 1985: 931-937.

Acknowledgements

Economic assistance for this study has been given by the Swedish Council for Building Research and by the Swedish National Road Administration.

ABSTRACT

The record shows that the emission of ammonia in The Netherlands is higher than that in the surrounding countries. Because of the ammonia emission's contribution of 30-37% to the acidification of water and soil an effort is made to find out whether this also applies to the acid deposition on monuments.

KEYWORDS

Erosion, acid rain, ammonia, sulphur dioxide, synergism, monuments.

THE SYNERGISM OF AMMONIA AND SULPHUR DIOXIDE IN THE EROSION OF MONUMENTS BY ACID RAIN

T. Stambolov

Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 8
1071 EA Amsterdam

Two objectives are the backbone of the workplan presented below.

To establish whether the ammonia emission's contribution of 30-37% to the acidification of water and soil in The Netherlands also applies to the acid deposit on monuments. For this, the profile erosion of monuments must be researched in the provinces Utrecht, North Brabant, Limburg and Gelderland, preferably with 500m of the emission sources. Comparison with the erosion profile of monuments in other provinces with less ammonia (e.g. North Holland, the church tower at Schagen) will have yet to show whether the acidification caused by ammonia is responsible for the increased damage to monuments.

To establish whether the rate of erosion of the monuments in The Netherlands shows any correlation with the emission of ammonia throughout the years 1870-1980 (see diagram). For this, inventory must be made of existing architectonic, art-historical, photographical and conservational documentation concerning the monuments used in the research.

In pursuing these objectives the following steps are important.

Weighted exposure-plates made from the sorts of stone used in monuments are attached to selected monuments and the water which drips off these is analysed weekly. This will indicate the composition of the rain-water and what was dissolved by the rain-water in the short duration of its contact with the plate.

The exposure-plates are rinsed monthly, every three months, every six months and annually, with double-demineralised water. The water is then analysed for any salts present. In combination with the weights of the plates which are to be measured weekly, this provides information not only about salts leached out of the stone plates, but also about other salts originating in the air pollution, such as gypsum, sodium sulphate and magnesium sulphate.

In laboratory tests the plates are exposed to air of an increased concentration of ammonia, with SO_2 present, in exposure chamber. These tests should give a definitive answer to whether ammonia synergistically active in the corrosion of limestone by sulphate aerosols (that is increased formation of gypsum).

The identification of nitrifying bacteria in monuments and the role in the nitrogen mass balance.

Characterisation of the test-plates with (electron)microscope in order to establish morphological changes brought about by air pollution.

The exposure-plates, which will have been exposed for one year, are bored out in order to establish the nature and depth of the weathering. The grindings are extracted with double-demineralised water and that extract is analysed.

As a control, exposure-plates made from a synthetic material are used.

The conversion of ammonia to nitrate (nitric acid) on the monuments can be measured quantitatively by the formulation of the nitrogen mass balance. For this, the exposure-plate is moistened with ammonium sulphate which has been enriched with nitrogen-15. The increase of nitrogen-15 in the run-off is determined and the result compared with the naturally occurring amount (0.3663%).

Measurements are taken of the pH, ammonium, chloride, nitrate and sulphate levels using the methods of flow analysis and ion-chromatography; sodium, potassium, calcium, magnesium, iron and manganese (the last two are catalysts in the oxidation of sulphur dioxide) are measured by atomic absorption spectrometry and emission spectrometry.

Archive research regarding the monuments in question.

Information about construction, any restoration work (including the materials used) and maintenance of the buildings.

Chronological inventory of available photographic material.

Annotated formulation of an erosion profile for the monuments in question.

Ammonia is the only gas in the atmosphere which reacts to counter-balance the acid gases carbon dioxide, sulphur dioxide and nitrogen oxides. Ammonia reacts with these gases to form the corresponding ammonium salts. In the case of wet deposition these reactions occur on the stone itself. The acid salts play an important role in this. Dry deposition, too, is significant in that regard.

It has not been proved whether direct damage to stone has been caused by ammonia. Indirectly, however, there are some mechanisms known whereby ammonia contributes considerably to the erosion of stone.

Ammonia reacts with both sulphuric acid aerosols and gaseous nitric acid to form respectively ammonium sulphate aerosols and ammonium nitrate aerosols. Ammonium bisulphate and ammonium sulphate are not only hygroscopic, but also deliquescent, and they absorb water at a Relative Humidity of 38% and 81% respectively, thus forming acid rain, which could otherwise not have formed.

This can also happen when ammonia reacts with gaseous nitric acid.

Wet deposition of ammonia in the pores of stone promotes the oxidation of sulphur dioxide by slowing down the drop in pH. This lowering of the pH is the result of the dissolved sulphuric acid. At pH values lower than 2 the sulphur dioxide gas no longer dissolves in the wet deposition containing sulphuric acid.

Ammonia, if present, raises the pH to 3, 4, or even 5. Within this pH range, sulphur dioxide is very soluble and its oxidation appears optimal.

Thus the formation of more sulphuric acid leads again to a lowering of the pH value, and the moisture in the pore is again ready to attack the stone.

Ammonia, neutralises the free acids present (sulphuric, nitric and carbonic acids), by forming with them ammonium salts. However, if nitrifying bacteria are present they convert these ammonium salts to nitric acid. Thereby for every ammonium ion two ions of hydrogen are released, and this contributes to the acidification in the soil: $\text{NH}_4^+ + 2\text{O}_2 = 2\text{H}^+ + \text{NO}_3^- + \text{H}_2\text{O}$

On the basis of this equation the so-called potential acid deposition can be calculated by increasing the deposition of free acid with twice the deposition of ammonium. It is thus assumed that the deposited ammonium is completely converted to nitrate. This is however disputed. Nitrification does not occur everywhere and moreover it is not a terminal reaction in acid conditions.

Nevertheless, ammonia does contribute ten times as much to the potential acid deposition, as the deposition of free acid. It has not yet been researched, however, whether this also applies to the contribution of ammonia to the acid deposition on monuments.

Acid rain generally contains more sulphuric acid than nitric acid. These acids attack stone and other inorganic building materials in various ways: sulphuric acid forms a crust of gypsum over the (lime-)stone which, depending on the concentration of sulphuric acid in the vicinity, determines the rate of the further desintegration of the stone. Nitric acid, on the other hand, forms very soluble salts and this provides a continual erosion of the stone material.

The contributions of sulphuric oxides, nitric oxides and ammonia or ammonium to the acidification of the soil and water are estimated at 45%, 22% and 33% respectively. Some experts use other figures, namely 31%, 33% and 37%, while still others give 50%, 20% and 30% as the average for The Netherlands.

The contribution of ammonia/ammonium to the acidification is expected to be between 30% and 37%.

Measurements show that the emission density of ammonia in The Netherlands is the highest in Europe (see map). The seriousness of this fact becomes clear when seen in connection with the relatively small area of the country.

Cattle are the most important source of animal ammonia release. The emission of ammonia from animal waste is less at night than by day and greatest in early spring. The provinces of Utrecht, North Brabant, Limburg and Gelderland have the highest concentration of ammonia emission (see map). That the neighbouring countries Belgium and West Germany, have been shown not to have such high concentrations of ammonia emission, probably bears a relation to the fact that ammonia is deposited in far greater amounts in the immediate vicinity than sulphur dioxide and nitric oxides. As a result, the contribution of ammonia to the acidification will be great in the area around the source. The guidelines in the ministerial publication "Ammonia and cattle breeding" reflect this clearly. Licences for housing development or extension of cattle breeding facilities within 500m. of such an area, may be granted only if the resulting ammonia deposit will not be higher than 130 mol/ha/year (new enterprises) or 2000 mol/ha/year (extension of existing enterprises).

The ammonia emission in The Netherlands in historical perspective:

Year	Emission of in tons x 1000
1870	30
1900	40
1930	60
1950	70
1960	100
1986	180

This shows that the ammonia emission is now six times greater than in 1870 and that the greatest increase occurred after 1950 (see diagram).

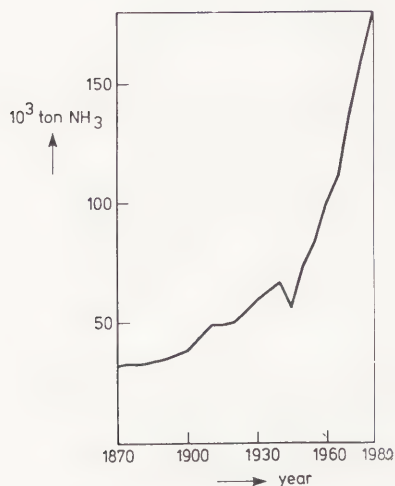
Ammonia and ammonium salts, once lodged in stone and brick masonry are both a source of alkalinity and the cause of salts mobility factors which are accountable for the poor performance of means, for instance some alkoxy silanes and siloxanes as well as the occasional failure of certain consolidating and water-repellent techniques used in the conservation of monuments.

Duration of the project

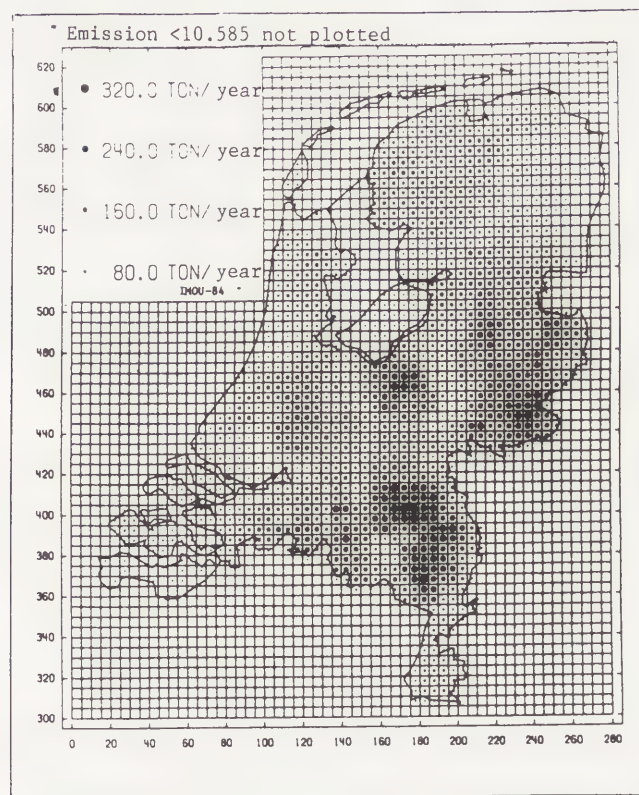
Three years, possibly to be extended to four or five years. That is because results from the measurements taken on the monuments will only be significant after field-tests of at least two years duration. However, even if such requirement is met it is not yet certain what period of time is necessary to obtain workable decisive results from such tests.

Bibliography

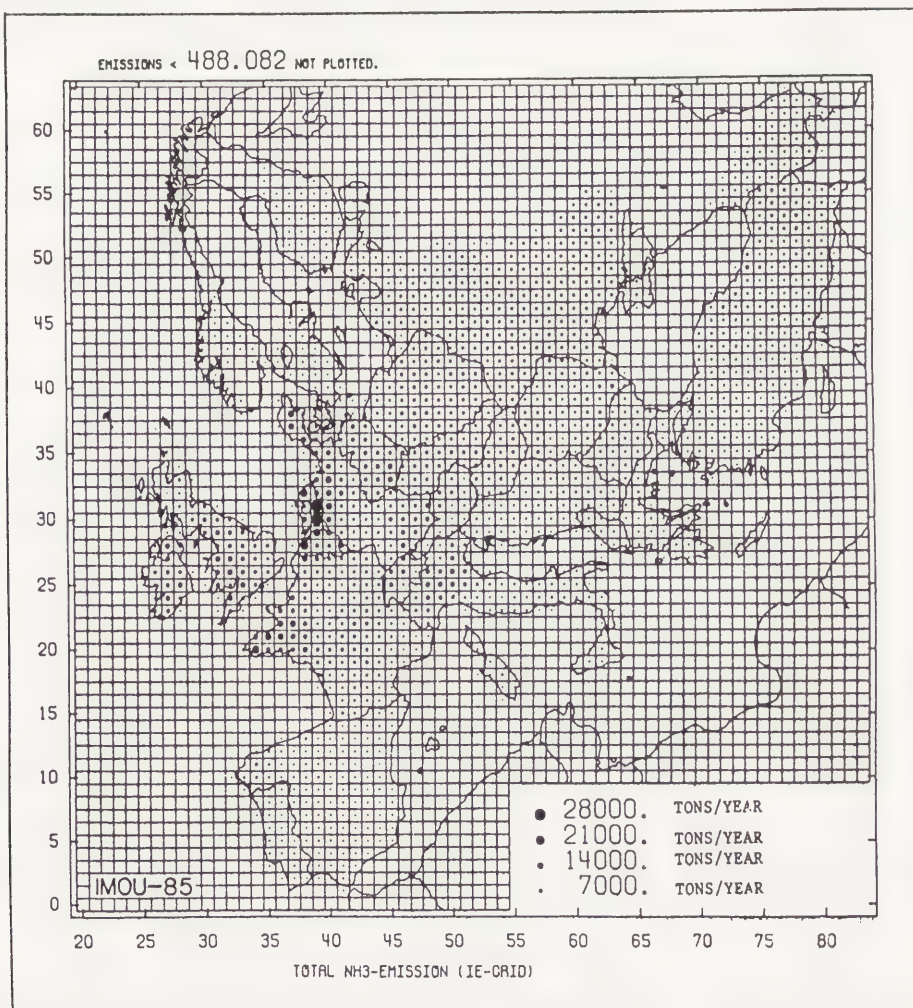
1. G.G. Amoroso, V. Fassina, Stone Decay and Conservation, (Elsevier, 1983), Amsterdam.
2. E. Buijsman, W. Asman, "Zure Regen", Chemisch Magazine, (December 1983), 654-58.
3. "Air Pollution and Conservation", Introductory information to an interdisciplinary symposium held in Rome, October 1985, 15-17.
4. W.B. Innes, "It's Raining Nitrates and Sulphates", ChemTech (July 1984), 440-47.
5. D. Onderdelingen, J.A. van Jaarsveld en N.D. van Egmond, "De Depositie van Zwavelverbindingen in Nederland", Lucht en Omgeving, no 3/4 (1985), 30-33.
6. A.J. Frantzen, R.L. Adolphs en W. Schipper, "De Chemische Samenstelling van de Neerslag in Nederland", Lucht en Omgeving, no 9/10 (1985), 132-135.
7. J. Slanina, "Measurement of strong acids and the corresponding ammonium salts in The Netherlands", VDI Berichte, 249 (1982) 177-182.
8. A.W.M. Vermetten, W.A.H. Asman, E. Buijsman, W. Mulder, J. Slanina and A. Wyers-Yperlaan, "Concentration of NH₃ and NH₄ over The Netherlands", VDI Berichte, 560 (1985), 241-251.
9. W. Asman, E. Buijsman, H. Maas, J.W. Erisman, A. Janssen, A. Wijers-Yperlaan en J. Slanina, "Ammoniak en Ammonium in Nederland en Europa", Lucht en Omgeving, no 5 (1987) 34-38.
10. K. de Winkel en E. van de Plassche, "Ammoniak-emissie reductie: Noodzaak en Mogelijkheden", Lucht en Omgeving, no 12 (1987) 125-127.
11. M.P. Keuken, "Effecten van Luchtverontreiniging op Monumenten" Energie Spectrum, 12, no 5 (1988), 104-114.



Historical ammonia
emission in the
Netherlands



Total -emission in The Netherlands per 5x5
km-grid



In Europe



Working Group 11

Theory and History of Restoration

Théorie et histoire de la restauration



ABSTRACT

The contemporary state of the restoration theory is characterized by a traditionalized desire to create a law-making concept turning a number of rules and methods to dogmas. The question of the authenticity of work of art, understood as identity, cannot be settled on the technological level alone, since authenticity is not just a physical category, i.e., the presence of matter, but also a relation, category of value, i.e., the presence of the meaning of a material structure. The recognition of authenticity takes place on the basis of a visual judgment which is mainly determined by the phenomenon of non-splitting consciousness. A visual judgment in turn depends on the specific features of perception, which an important part played by mechanisms of visual identification of information areas (or gestures) and correlation of images (objects) under the effect of visual illusions (e.g., Piaget's effect). Psychological processes are aimed at regulating the object perceived. Putting a structure in order is the fundamental property of perception, visual judgment, thinking and practice, hence, restoration interference can be assessed as the means of putting in order the structure of a work (artistic, meaningful and material) or, to be more precise, finding the order laid down in it.

KEYWORDS

Psychological purpose, visual perception, interpretation, actualization, historical principle, quality of the art object, image.

THE LAWS OF PERCEPTION AND REGULARITIES OF RESTORATION OF ARTISTIC MONUMENTS

Yu.G. Bobrov
Repin Institut,
17 Universitetskaja nab,
199034 Leningrad,
U.S.S.R.

Introduction

Restoration always implies a certain interpretation of works of art. This statement is paradoxical in that many advocates of a strictly scientific approach seek to exclude the very idea of interpretation is not and must not be the purpose of restoration. Nevertheless, it is an essential feature of the functioning of culture, a method of intersubjective interaction. Culture, in contemporary understanding, is defined as "a joint method and product of human activity realized in objectification and dis-objectification processes and emerging in an objective form linking these processes..." /1/. It is natural to proceed from the fact that restoration is a specific form of activity in the course of which artistic cultural heritage is realized, it, therefore, being part of this process. In turn, from a philosophical point of view, activity is "an actual reality of subjective-objective relations, a combination of all forms of activity of interacting subjects aimed at the objects of the outer world..." /2/. The starting point of activity is intercourse on the level of perception. Indeed, not only any conservation or restoration act, but also any judgment is a determining action, emerging from the act of perception of work of art. In conformity with the general theory of thought it is necessary to recognize "polymorphism" of thought processes which link together inner theoretical and sensual activities, thought and practical action /3/. Human perception is not a mechanical process of passive reproduction, but on the contrary, a personal, motivated and purposeful process. Psychological investigations conducted by D.N. Uznadze and his disciples demonstrated convincingly that "sensual content is not predetermined by an irritant once and forever; it depends primarily on the significance the examinee attaches to the exhibited object" /4/. This proposition becomes of a particular significance when a work of art or any other cultural monument acts as an object, since we give it certain values by recognizing it as such. So, we have a work of art facing us. In order to realize its artistic message, cognitive and other meanings, it is necessary first to feel, to perceive, the form. Let us suppose the form is the material structure with all its specific characteristics (a degree of preservation, a correlation of the original and that introduced later, etc.) which, being an organized matter, at this point is acting as an object of visual perception. In the course of perception in man's conscience a certain psychic condition emerges, determined by the sensual phenomena and qualities of the object. It is, however, not a fully accomplished emotional experience at the initial stage. For its concrete formulation a moment of recognition of the object perceived by the subject is necessary, which is possible only after he has comprehended the meaning, i.e., first of all, we answer the question "what is this?", it concealing personal interest that forms perception in a certain direction. And this takes place on the level of subconscious.

The observation of psychic conditions formation processes enabled D.N. Uznadze to draw a fundamental conclusion that the subject, under the effect of the object, acquires a special emotional psychological aim which is "the condition of consciousness of the meaning of the object" /5/. In turn, consciousness of the meaning can emerge only from the knowledge accumulated in previous experiences and on the conditions of subjective and objective nature: the requirement, as well as the situation in which it can be satisfied. The repetition of emotional experiences, satisfying a person, leads to the fixation of the aim (its generalization) which begins to noticeably affect perception as a set stereotype. The process of man's vigorous emotional and intellectual activity forms a multitude of aims mutually affecting one another which, after having been fixed in the psyche, turn into aims of a higher form on the level of thinking. In so doing, their interlevel mutual correlation is going on. Each person can feel the effect of this mechanism in his own perception when an unconscious negative reaction, say, to unpleasant colour combinations causes the rejection of a picture or, vice versa, consciousness of an artist's significance according to "the table of ranks" gives rise to positive emotions with simi-

lar qualities of a work of art. The stereotype often obstructs the emergence of a psychological aim adequate to the object. This phenomenon manifests itself in the so-called preconceived judgments which are more common in the study of art than it might seem. The establishment of authenticity of a disputable work of art is sometimes based fully on psychological stereotypes. Thus, a well-known embarrassing situation occurred in 1984 when two sculpture heads were found on the bottom of a street canal in Leghorn, which were taken by some experts for genuine works by Modigliani. The psychological aim, reinforced by the interests of the organizers of the exposition "New Modigliani: Years Devoted to Sculpture", induced them to see in the hoax, perpetrated by several students, "indisputable signs" of the creative manner and style of the world famous artist. No less impressive are stereotypes established by fixed aims not only in the assessment of restoration operations, but also in the formation of restoration methodology. For instance, "dotting out" losses technique, introduced back in the 19th century, could have been implemented into practice only after emotional recognition of the experience of impressionism.

Thus, the psychological aim contains an unbreakable unity of inner, subjective, state of personality and activity as the outer expression of the aim in a conduct. In so doing the aim determines action not rigidly but within probability.

The restorer, like any other individual, perceives works of art by sight. This is, however, a simplified impression. In fact visual perception is a sum total of a complicated interaction between eye and brain. The investigations of the physiology of visual perception showed a noticeable effect of the psychological aim. What we see is not just a reflection of the object on the retina, but a kind of composition of this particular moment information and memory traces. It is not by chance that R.L. Gregory, one of the leading specialists in this sphere, said: "The sentence 'I see what I understand' is not a children's pun, it points to the connection that really exists" /6/. Perception is a dynamic search for the best interpretation of the existing information. Of principal significance to us is a systematizing principle of visual perception as a fundamental property. In the mechanism of image perception there are distinct phases of general viewing and long-term fixations on maximum informative areas or extremes of informativeness /7/, which form the so-called *gestalts*. Perception does not amount to simple mechanical reading of images by details. These visual blocks are compared to one another resulting in many illusions. There exist illusions in the perception of portrayed space on a plane, of colour and tone contrast, of configuration and dimensions of linear forms depending on the mutual impact of elements constituting them. Fixation points are always located not at the outline but in the center of gravity of spot, i.e., the eye estimates the form first of all, dimensions may seem larger or smaller depending on the condition of the surface, which attaches a special significance to all elements of the form introduced later (losses, dents, insets, various kinds of conditional, standing out, additions) which are thus not only documental evidence, but also active agents of the formation of a visual image. On the whole visual distortions can reach 20%, and that is why any addition of some or other details to the image can have a substantial effect upon the image system of a work of art /8/.

All this gives reason to claim that peculiar types of image processing (emotional interpretation, systematization, symbolization and the like) are carried out on the level of the psychological aim and manifest themselves in the psychophysical mechanism of visual perception. Thus, in the object subjectivation process there is a moment of certain interpretation which means "explanation", "exposition" (from Lat. *interpretatio*). Hence, interpretation acts as an objective regularity of actualization process, i.e., transference of the object from the potential to actual state going through the levels of perception, contemplation and thinking. Actualization as a condition of activity is carried out only if there is a requirement arising from a combination of subjective and objective conditions. It seems evident that we can regard a restoration act as both social and personal requirement. And whereas on a personal plane requirement is determined by the motive, i.e., "realization of the advantage of value to myself" /9/, and, consequently, its justification, social requirement is formulated on the level of thinking by way of realizing the goal. Motives are not in actual fact realized by the subject: "when we commit some or other action, we do not usually account for them to ourselves at this moment", A.N. Leontiyev writes, "it is easy for us to motivate them, but motivation does not always contain an indication of

their real motive" /10/. By combining individual motives and correcting them into a social requirement we obtain a verbalized, i.e., expressed by the conceptual logical apparatus, model of a proposed result. This model is, on the one hand, determined by the object, and on the other hand, it is its interpretation. In other words, proceeding from the recognition of the inner unity of intellectual and sensual spheres it is necessary to consider interpretation as an essential moment of subjective-objective relations emerging in the course of any activity, including restoration. Thus interpretation proves to be an objective regularity of the restoration effect upon cultural monuments.

Now let us turn to another link in the activity structure: the object. At this point it is necessary to recollect the fact of non-identity of a work of art in the course of its historical existence /11/. Firstly, natural ageing of matter leads to irreversible changes in the form. Secondly, everything that can be included in the complex of time traces, spots, losses, form degradation, later non-authorial layers, additions, alterations, restoration interference results and the like, also render a work of art different from its original appearance. Correspondingly, the course of time increases a share of new emotional associative complexes in perception and inadequate interpretation. Thirdly, as it is included in a different culture, changes are taking place in the social functioning of a work of art; the disappearing functions are being replaced by new ones, or concealed ones are revealed. Thus utility objects are given the significance as works of art and cultural monuments, the theological dogmatic meaning is "washed out" from works of religious art by a rise in purely artistic value. There is quite a peculiar change in the functioning of architectural ruins which in their form, idea, artistic expressiveness and designation are least of all identical to their original state. A natural process of a rise in non-identity can be halted by means of conservation, i.e., restoration interference, but only with respect to the preservation of form. Historical changes in the quality and being of an object can be defined as its non-subjective interpretation, i.e., not being the consequence of activity of the given individual perceiving it, but emerging under the effect of inner and outer causes. One can see in these changes a well-known similarity to the interpretation to which an object is subjected in the course of perception.

A question arises as to the limits of growing non-identity and ways of approaching an adequate state, understanding and use of a work of art. There are several stages marked in the course of actualization on the way of transferring the object from a "thing-in-itself" to a "thing-for-us" state /12/. Already the level of perceiving a work of art acquires significance by being included in the context of contemporary culture. The recognition or non-recognition of the value of a work of art takes place in accordance with the results of comparing the meanings of individual and sociocultural codes. Then understanding, comprehension of the message, meanings, style and logic of form occur on the value cognition level in the author's context and in the context of that period. And that "intersubjective interaction", according to M.S.Kagan, which creates "the crossing of two semantic fields in one work of art" happens at this stage of in-depth comprehension /13/. Interpersonal intercourse is, however, part of a dialogue of cultures. For communication to take place several conditions are required: the presence, in this case, of material information carriers, their revelation and recognition as such, finding of a reliable adequate meaning and comprehension of the meaning. Thus, interpretation is confined to the genuine meaning as there can be no intercourse outside the preservation of meanings. The identification of the authentic is possible only on the basis of understanding historical changeability of interpretations, i.e., of the approach to a work of art from the standpoint of historicity and its interpretation in terms of the history of art as was noted by A.A.Gornfeld at the turn of the century /14/. The historical aim, as Ch.Brandy defines an approach from the standpoint of historicity, rests upon the objective socially conditioned criteria of culture. It plays an important part as a restraining objectivizing factor both on the subjective level, participating in the formulation of the psychological aim, and on the intersubjective level, giving the authentic matter of a work of art, and its message and image system the significance of documental value. It should be emphasized, however, that the principle of historicity is not an alternative to interpretation, but forms its part, one of its manifestations, as understanding, say, of a mosaic on the floor of a Roman bath as a document of the period was not proposed by the author, but is a consequence of our interpretation. In real human activity personal and social aims are mutually conditioned

but, in so doing, do not always fully coincide.

Preserving the authentic meanings of a work of art, thus avoiding arbitrary interpretation, is possible only by preserving its authentic material substance. Therefore, the technological quality of restoration interference in the material structure should be regarded as the second factor. It is the criterion of quality of preserving or revealing (disclosing) the authentic form that makes it possible to judge on the reliability of communication perceived.

Conclusion

At least several problems arise in connection with the notion of authenticity. One of them is the necessity of bringing into correlation of historical and aesthetic values, since there can be no documental self-value of matter in an artistic monument outside the really authentic artistic meaning which alone turns matter into form. There is no need to prove that an artist's intention is the law of designing a work of art and determines such regulation of form which links all the structural elements into an integral system. This inner unity of each particle of matter can be regarded as potential, but actual, i.e. it becomes real only when in the course of perception we are aware of each individual element as part of general regulation, which does not necessarily require the physical presence of form in the full original volume. The studies of the psycho-physical mechanism of visual perception showed that aesthetic emotional experience arises owing to psychological aims orienting perception to search for the inner regulation of an image /15/. It is emotional preference, given unconsciously to a structured form, that gives rise to a sense of satisfaction which is subsequently verbalized on the level of thinking as the understanding of the artistic value of an object. (This was the ground for L.S.Vygotsky to assert that "thought itself is born not by another thought but by the motivating sphere of our consciousness" /16/. Thus an aesthetic emotion, followed by an aesthetic aim, precede the understanding of the historic value of an object. Since aesthetic attitude is objective and "covers certain aspects of any of the existing types and kinds of human activity" /17/, one can claim that the unity of historical and aesthetic interpretation is the second regularity of restoration activity. Interpretation on the aesthetic level is confined to, and directed by, the objectively existing regulation of form. Hence, adequate evaluation can be made when the authentic potential unity of all parts of a work of art is preserved as a result of the restoration effect. Features of regulating activity are present both in the very act of recognizing the values of an object and giving it meanings, and in the operations on conservation, revelation and compensation of losses. This gives us reason to believe that restoration contains not just certain, but precisely regulating interpretation of an object. The return to the original appearance, like mummification, denoting the fixation of the status quo, is only illusions giving food for arguments about restoration.

Bibliography

1. M.S.Kagan. "Art as a Phenomenon of Culture".- In the book "Art in the System of Culture", Leningrad, Nauka, 1987, p.9
2. M.S.Kagan. "The World of Intercourse. The Problem of Intersubjective relations". Moscow, Politizdat, 1988, p.89.
3. See: A.N.Leontiev. "Activity. Consciousness. Personality". Moscow, 1975; "Thinking". The Voprosy Filosofii Magazine. 1964, NO.4, p.89.
4. D.H.Uznadze. "Psychological Studies". Moscow, Nauka, 1966, p.3
5. Ditto, p.47
6. R.L.Gregory. "Eye and Brain. Psychology of Visual Perception". Moscow, Progress, 1970, p.17
7. See: G.T.Busswell. "How People Look at Pictures". Chicago, 1935; N.V.Zavalishin, I.B.Muchnik. "Models of Visual Perception and Algorithms of Analysis of Images". Moscow, Nauka, 1974
8. Ditto, p.119
9. D.N.Uznadze. "Psychological Studies", p.400
10. A.S.Prangishvili (edit.), A.E.Sheroziya, F.V.Bassina. "Subconscious. Nature, Functions, Study Technique". Tbilisi, Metzniyereba, 1978, vol.III, p. 342.
11. See: Yu.G.Bobrov. "Certain Theoretical Aspects of Restoration of Works of Visual Arts". Artistic Heritage. Storage, Study, Restoration. VNIIR, issue 10, Moscow, 1985.
12. See: S.L.Kropotov. "Actualization as a Regularity of Historical Artistic Process". Art in the System of Culture. Leningrad, Nauka, 1987, pp. 123-128.

13. Ditto, p. 128
14. A.A.Gornfeld. "On Interpretation of a Work of Art".
Russkoye Bogatstvo, 1912, N° 2, p.171.
15. See: D.G.Berlyne. "Measures of Aesthetic Preference".
- Psychology and Visual Arts. London, 1970.
16. L.S.Vygotsky. "Thought and Speech". Moscow, Leningrad, 1934,
p. 314.
17. A.N. Iliadi. "Formation of the Aesthetic Sphere of Human
Activity and its Practical Nature".- Problems of Ethics and
Aesthetics, issue 2. Nature of Art and Mechanisms of Artistic
Activity. Leningrad, LGU, 1975, p. 23.

ABSTRACT

In the modern museum world there is a need for understanding between conservators and curators whose common goal is the preservation of both the meaning and physical substance of works of art: I call this activity "custodianship". This paper describes a project to reconstruct the nineteenth-century roots of the present professions of conservation and curatorship and to apply this information to the training of museum professionals.

KEYWORDS

Sir Charles Eastlake, science and nineteenth-century art, conservation as interpretation, Victorian museums

HISTORY OF CONSERVATION AND THE TEACHING OF MUSEOLOGY

Barbara Whitney Keyser
Instructor, Museum Studies Program
University of Toronto
468 Brunswick Ave.
Toronto, ON M5R 2Z5
Canada

The Project

Conservation is more than a set of physical preservation techniques. It is also an interpretive activity which involves a complex of artistic, scientific, and historical ideas which influence the approach to treatment whether they are acknowledged or not. Rather than deny that conservation and exhibition of works of art are inevitably interpretive, conservators and curators alike must embrace their complementary roles in preserving both the physical substance and meaning of the works. Ernst Cassirer ascribed great significance to the historian's role as keeper of the collective memory of humanity.¹ I would like to add that not only is there a need in the culture as a whole for a sense of continuity, which is the function of museums; but within the museum profession there is likewise a need to know where we have come from in order to understand what we are doing and to help us make informed choices.

Therefore my reconstruction of the intellectual as well as the technical context of nineteenth-century custodianship has a threefold purpose. The first is to show how the museum professions developed, the second is to show how nineteenth-century custodians thought about and interpreted their "old masters", and the third is to illuminate the context of creation of their contemporary art so that we can be better interpreters of nineteenth-century works.

Since this enterprise involves the relationships between art, science, technology, and museums, the topic is clearly enormous. To make it manageable, my research focuses on the period 1780 to 1860 and, specifically, on the career of a single individual, Sir Charles Lock Eastlake (1793-1865).

One might ask, why this period and why this individual? The answer to the first question is found in the histories of the component intellectual disciplines of chemistry, art history, and art theory (especially colour theory), as well as the activity of art patronage and connoisseurship. All of these developed dramatically between 1780 and 1860 when they emerged in recognizably modern form. With Newton's *Opticks* as a starting point, eighteenth-century investigators studied problems of colour mixing, debated the nature of primary colours, began to study "subjective colours" and contrast phenomena, and attempted to describe and order colours systematically. By 1780 art theory reflected these investigations in ideas of colour harmony and accurate representation which had scientific rationales. Also, in 1780 art history emerged as a systematic and historically accurate discipline, beginning with Winckelmann's archaeological approach to antiquity. His method also had close ties to the methods and aims of natural history.² These ideas began to affect restorers who started to think in terms of historical accuracy rather than re-making works to the past to suit current taste. This approach to art of the past created interest in scientific investigation and analysis of the techniques of the past. And it was also in the 1780's that chemistry emerged as a science with the power to undertake such analyses and contribute to the industrial revolution. Building on eighteenth-century studies of chemical causes of colouring and bleaching at the Gobelins, a distinct body of literature on the permanence and history of painting materials appeared in the 1820's, as did the first specialized restoration treatises.³ 1860 marks the close of the transition period of the component disciplines. In colour, Helmholtz resolved the problems of colour vision and colour mixing and his findings together with Chevreul's were being applied to painting and aesthetics. Schnaase declared that knowledge in the field of art history was complete, and the discipline was institutionalized in German universities. Organic chemistry was systematized, and the age of organic synthesis was beginning. And art collecting, creation, and patronage had been transformed from aristocratic activities to public ones with strong connections to industry.

Eastlake's interests and activities mirrored those of his milieu. He was a painter, art theorist, art historian, connoisseur, educator, curator, and administrator. His wife Elizabeth was also an art historian and arbiter of taste. Eastlake's circle included eminent scientists: he consulted Faraday regarding museum climatology and enclosure of paintings to prevent deterioration. Eastlake's own interests in color theory and the properties of painting materials were manifest in his translation of Goethe's *Farbenlehre* and authorship of *Materials for a History of Oil Painting*. He studied the German art theorists and historians and translated their works. Many of them, such as Waagen, were also his colleagues. In addition, he testified in Parliament during the treatment controversies of the 1850's, surveyed restoration practices on the Continent, and experimented with Pettenkoffer's regeneration process. He also knew Morelli, whose "scientific" method of attribution was derived from his study of comparative anatomy when he was a medical student. Eastlake himself studied the works of Edward Forbes and D.R. Hay, who sought rational theories of design to meet the aesthetic challenge of machine-made decorative art objects.

Thus the scope of this project is wider than the "internal" histories of conservation which have been written already.⁴ Placing history of conservation in an intellectual and institutional context, I have divided the topic into three divisions, each with two chapters. In each of the six chapters, I will discuss Eastlake's activity in the area; the activities of his associates; what he studied or read on the subject, which can be ascertained through the published catalogue of his library and the literature he cites in his writings; the kind of interaction of the disciplines involved; the problem addressed or solved in the activity; and a bibliography of primary and secondary sources.

To describe the kinds of interaction between art, science, and technology precisely, I will apply a typology which I developed in another paper.⁵ The kinds of interaction are the following: application of the method of descriptive science; the prestige of science as the most certain form of knowledge which can and should justify aesthetic theories and improve artistic products; the ideology that science should be used to solve technological problems; application of experimental methods to technical problems; application of specific scientific theories or ideas (including biology as well as chemistry and physics); hierarchical or deductive ordering of knowledge; and natural science as a source of metaphors, analogies, or methodological models for cultural scholarship.

The first division covers influences moving from science and technology to art. The first chapter is chemistry and the visual arts, which encompasses study of past materials, including analysis of them; investigation of the permanence of new materials including measurement and testing of photochemical effects in deterioration of materials; development of new materials as applicable; application of this knowledge to the preservation of existing works; application of chemical knowledge to better fabrication of new works of art; and chemical knowledge as part of artists' training. The second chapter is nineteenth-century industrial technology in the service of museums. This includes lighting technology; environmental studies including the study and measurement of light and humidity, in the context of contemporary meteorological knowledge; and methods of heating, cooling, and ventilating. Another aspect of technology in the museum is photography as a documentation and study technique.

The second division covers influences from art to science, technology, and industry. The third chapter examines Victorian theories of art and design with emphasis on the search for "laws" of form based on geometry, crystallography, and biology. The impact of the industrial revolution, resulting in the creation of new art forms and the Victorian crisis of taste in fine art and art manufactures are other aspects of nineteenth-century art which conventional histories have not emphasized or treated sympathetically. Still another is the application of colour science to theories of colouring in painting and the decorative arts. The fourth chapter examines the relationship between museums and industry: public support for museums, including fine art museums, was based on museums as repositories of examples of good taste and design for industry. International exhibitions of art manufactures such as the Crystal Palace of 1851 are another example of the intimate relationship between industry, technology, and the growth of museum-related disciplines.

The third division covers the function of museums as the public trust for scholarship and preservation. It is in this area that museums take on their modern character as custodians and interpreters of cultural heritage. The fifth chapter concerns science and the discipline of art history: that is, the tasks of ordering and interpreting the art of the past. The German sources of Eastlake's ideas, such as Kant, the Schlegels, Lessing and associates like Waagen and Kugler are decisive here. I plan to trace out their connections with scientific thought, beginning with Kant's pervasive influence on the philosophy of biology, art, and history; German idealism in artistic and scientific thought and its modification by the English; and the relationship between natural and cultural sciences as well as between works of art and works of nature. The connection of natural history and historiography generally is strong: examples include ideas of morphology, development (embryology), classification, and the comparative method. However, they have been little studied. I believe that pointing out the pervasion of scientific thought in the foundations of art history will counter the modern notion that the two are antagonistic.

The last chapter discusses the rationale underlying nineteenth-century conservation treatments. Here the key question is not so much the actual techniques, which have been documented, but whether and how nineteenth-century theory and historiography of art affected evaluation and presentation of art of the past. This includes technical aspects as part of the "scientific" study of past art and as a source of insight into what artists had tried to do technically and aesthetically. Another key question is how nineteenth-century art theory, especially the canon of complementary colours which became current around 1800, affected views of what past artists were trying to achieve, and whether and how curators altered their ideas of presentation including cleaning, framing, and arrangement of works in galleries, to correspond with their conceptions of art history and theory. The problem of establishing "objective" criteria for condition and authenticity also arises at this time.

Application

By reconstructing the relationship of artistic and scientific ideas in the nineteenth century, I believe understanding of our own rationales for our activities today will become clearer. For the present separation, even antagonism, between art and science has blocked the investigation of the impact of scientific ideas on art, and obscured the relationship between the disciplines of conservation and curatorship. There are two negative consequences of this neglect. The first is that the importance of scientific ideas in the development of the visual arts in the nineteenth century has been deleted from art history and we have thus been deprived of a full interpretation of the meaning of the works.⁶ The second is misunderstanding between conservators and curators as reflected in modern treatment controversies and institutional tensions.⁷

My approach to history of conservation as idea as well as technique was inspired by a call from within the conservation profession for the application of history and philosophy of science and technology to the activity of conservation to counter-act attacks on the profession from other museum workers.⁸ It also promotes the concept of custodianship as the area of modern museology in which curatorial and conservation concerns and expertise overlap.

In October, 1989, the National Gallery of Canada held a symposium called "Shared Responsibility" which successfully focused the common conservation or physical preservation concerns of exhibitions from the perspectives of the artist, conservator, scientist, and administrator. I believe the concept of the exhibition as shared responsibility can be extended to include the ensemble of physical preservation and the preservation of the meaning of works of art. The exhibition, whether temporary or permanent, is the middle term between the practical and intellectual operations of museums. This is precisely the field covered by the term "custodianship".

It is heartening that increasing numbers of museum professionals are being trained in museum studies as well as their specialist academic field. I hope that my research can become an effective tool for such training. By giving custodianship a philosophical structure and historical content, I plan to make it a discipline, so that a unified approach to it can be communicated to future art historians, curators, conservators,

administrators, and scientists.

All of these personnel are custodians, and their activities fall into three overlapping areas: management, technology, and interpretation. To ensure mutual cooperation, respect, and optimal physical and intellectual care of objects, each should know something about the other. Clearly, all must receive some training in management. This includes not only knowledge about present institutions, but also a historical perspective on museums and the public; art history, taste, and patronage; conservation practice; and applications of science and technology to museum problems. Also, those whose concerns are primarily intellectual benefit from knowledge of practical and physical aspects of collections, and vice versa. Every curator should understand the fabrication of works of art, examination techniques, treatment options, assessment of condition, and preventive care. In my opinion, there is a great potential for the use of history of technology in the interpretation of objects to the public; thus the study of materials and technique can be both practical and interpretive. Curators need not be so knowledgeable in such technical areas as the materials and techniques of remedial treatments or research in materials science, as it is part of the responsibility of the practicing conservator and conservation scientist to communicate the results of research in these areas to the curator.

On the other hand, it is equally beneficial that conservators and scientists be well-informed about the interpretive aspects of object presentation. Part of the sensitive choice of a treatment includes a historical perspective on conservation and its place in museums as well as the history and philosophy of science, which creates a healthy appreciation of science's limitations and respect for sound methodology and design of experiments. Interpretation also includes the art-historical questions of authorship and influence, oeuvre of the artist, cultural significance of a given work over time, and the history of appearance factors and taste. Some of these issues, especially the last two, have not been addressed even by art historians. Unravelling the context of creation of works of art as revealed in a combination of technical examination and study of historical texts on art theory could provide an extremely potent tool for choosing an appropriate way to present a given work or ensemble of works. Collaboration between conservators and art historians could be very fruitful here.

Conclusion

Presentation of cultural property in museums involves both the technology of preservation and interpretation of the works as mediators between the present and the past. These aspects of their care should not be separated, and together they comprise the custodianship of works of art. Technical aspects centred on the object include materials, technique, fabrication technology, condition, preventative care, and remedial treatment techniques. Interpretation includes history of museums, history of taste, history of conservation, history of art scholarship, and contributions from scientific thought. Just as there is no interpretively neutral writing of history, there is no interpretively neutral conservation treatment or exhibition of cultural property. Therefore, understanding and collaboration between technical and interpretive museum professionals, based on understanding of how the disciplines pertaining to custodianship came into being, is necessary so that informed choices of presentation of works will be made. Then the meaning as well as the physical substance of works of art will be preserved.

Endnotes

1. Ernst Cassirer, Essay on Man (New York: Doubleday, 1953), 223-234.
2. See Wolf Lepenies, "Johann Joachim Winckelmann. Kunstgeschichte und Naturgeschichte im achtzehnten Jahrhundert" in Thomas W. Gaehtgens (ed.), Johann Joachim Winckelmann 1717-1768 (Hamburg: Felix Meiner Verlag, 1986).
3. Cornelia Wagner, "Die restauratorische Bibliothek im Jahr 1828", Kunsttechnologie und Konservierung 1988 2, 336-344.
4. Because the groundwork has been laid, it is not necessary to repeat the process, but rather to build on such works as Alessandro Conti, Storia del restauro e della conservazione delle opere d'arte (Milano: Electra Spa, 1988) and R.-H. Marijnissen, Degradation, conservation et restauration de l'œuvre d'art (Brussels: Editions Arcade, 1967).

5. Barbara Keyser, "Between Science and Craft: The Case of Berthollet and Dyeing", Annals of Science, in press.
6. For example, Rosen and Zerner suggest that progress in the historiography of nineteenth-century art will come from examination of interactions of art with social and technological change rather than reviving the reputations of individual minor artists. See Charles Rosen and Henri Zerner, Romanticism and Realism: The Mythology of Nineteenth-Century Art (New York and London: W.W. Norton & Co., 1984), p. 106.
7. For example, see Mansfield Kirby Talley, "Humanism, Restoration, and Sympathetic Attention to Works of Art", The International Journal of Museum Management and Curatorship 1983 2, 347-353.
8. Phoebe Dent Weil, "'Visually Illiterate' and 'Historically Ignorant': The Need to Re-examine Art Conservation's Humanistic Foundations", AIC Preprints 1984, 86-93.

ABSTRACT

The paper is devoted to the problems of ethics in Russian and Soviet restoration based on the old Russian and easel painting. Problems of ethics are particularly topical in restoration which is linked to many sciences and to moral problems.

KEYWORDS

conservation, restoration, storage, painting architecture.

PROBLEMS OF ETHICS IN RUSSIAN (19TH CENTURY) AND SOVIET RESTORATION BASED ON NATIONAL PAINTING MATERIALS

L.I. Popova
10 Krestyanskaya Pl., 109172, Moscow
VNIIR
U.S.S.R.

Introduction

As is known, ethics in everyday life is a principle corresponding most of all to man's conduct under the given conditions. The ethics of a scientist has an even more precise and restricted scope: his conduct should invariably rest upon the existing level of science and cannot run counter to it. Problems of ethics are particularly topical in restoration which is linked to many sciences and, most significantly, to moral problems. We shall endeavour to observe their evolution on several differing in time and heterogeneous phenomena that have occurred and are occurring in national restoration. Nowadays, having lost a significant number of cultural monuments, we feel particularly acutely how topical the problems of ethics are in the sphere of culture. This is a hundredfold so concerning the problems of restoration, since what has been done by means of it is irreversible and results in valueless losses in the cultural heritage of the people. The facts cited below demonstrated at a certain period a non-ethical approach to the protection of monuments only; at a later period when restoration began to be transformed into science, a non-ethical use of its discoveries. Like any other science, the science of restoration cannot by itself be either moral or immoral. These definitions were in the 20th century linked to the nature of the use of achievements in the entire complex of research, particularly in the sphere of aesthetics. But in the mid-19th century, the period from which our paper begins, as is shown by the facts, the activity in the protection of monuments in Russia, including restoration, was directly dependent upon the moral climate of society and the level of its ethical norms stemming directly from the development of the study of ethics and of art. It was no accident that its rise in the pre-revolutionary period occurred at the turn of the century and in the first decade of the 20th century when the Russian intelligentsia was looking forward to the coming social and political changes. It was in this period that art studies began to include new strata of national art, both ancient and new, which ensured subsequently a quite certain place of Russian painting in the context of world culture.

But sometime earlier, in the 1840s-60s, when religion no longer contained in itself, as was the case before, philosophy, science and poetry, and it turned into a no less official institution than the bureaucratic empire, monuments suffered more not from the external, but internal, enemy. "What was spared by the tars and fire", A.K. Tolstoy wrote in a letter to his former pupil, Czar Alexander II in 1860, "it (the higher clergy - L.P.) undertakes to destroy" /1/. Sometime later, early this century, N.N. Wrangel, a prominent Russian art historian, explained the horrifying destruction of architectural and artistic monuments (mostly churches) in the 1840-60s follows: "The point is that people, who had hardly grasped the elementary essentials of historical science, took it to their head that they knew all and destroyed without any hesitation what was outside their sphere of knowledge". Among such people was, he justly thought, Emperor Nicholas I in whose epoch the politicization of art occurred on the one hand, and, on the other hand, "there were committed ... most outrageous acts of restoration, 'according to new formulae', of ancient monuments" /2/, and at the same time a great deal was destroyed under the pretext of "a historical evaluation"; A.K. Tolstoy brought charges first of all against the clergy.

The past is frequently being idealized, and the interest of descendants in the antiquities is followed by large-scale protective action purported to be taken by people having not only a high artistic taste, but also aesthetic knowledge. The interest in ancient monuments, however, resulting from the people's spiritual and aesthetic activity brought about in the 19th century a reverse process, which compelled the above-mentioned Tolstoy to exclaim: "And all this senseless and irreversible barbarity is being perpetuated all over Russia before the very eyes and with the benediction of governors and higher clergy" /3/, among whom the highest position was occupied by the Metropolitan Philaret, about whose "historic" knowledge the great writer expressed doubt: "one can recognize the Raskolniks (schismatics) as more

enlightened than the Metropolitan Philaret" /4/.

There were real grounds for this statement. In fact without the slightest doubt, on the Prior's order, ancient frescoes of a 12th century church in Staraya Ladoga were broken off with a sledge hammer to be replaced with a wall painting more in their taste when the attitude to the spiritual and moral force of religious painting was said to have changed completely: aesthetics dealt with secular art (first academic and later democratic art) where as ancient church painting had as yet no "valuable" price and ethical norms relating to its protection, as one can see, stood at the lowest level. The spirit of medieval church painting was broken once and for all, and the development of art reflected then not so much ideas common to all humanity and life (in the broadest sense of the word), but rather everyday life. Turning to new and more topical problems of the period aesthetic thought retreated from religious ones leaving official art and the protection of monuments to the higher clergy (by no means always competent) and, above all, to the chief patron of art, Czar Nickolas I, a man who was quite ignorant in the matter of art. Suffice it to say that he ordered paintings to be finished to his taste, attributed pictures personally and destroyed for some or other reasons, ranging from political ones to those of taste, objectionable works of art of various kinds (from painting to jewelry) setting an example of ethical norms in the sphere of the protection of cultural monuments, and in social life as well.

Spiritual principles in all spheres of official culture yielded ground, and the restorers, employed to execute large governmental orders, stopped treating their finest handwork art as a sacrament. And most icon-painters themselves ceased to be zealous of spirit. They raised to a standard level of perfection, attained in the past periods what was congenial to their social and cultural orientation while distorting all that was alien to their views of life regulated to a tremendous extent by the system of government. "When priors are asked about the reasons for all this destruction and injuries, they answer proudly that all these 'delights' were made possible by well-wishing donors, and add with contempt: "One should not be sorry about the former, it was old!" /5/. Thus, ethical problems, not raised by scientific aesthetics, led to false results in the sphere of the protection of artists monuments.

A peculiar acid test reflecting ethical norms of the 19th century restoration, as well as of the post-revolutionary period, became the greatest monument of Kiev Russ, a monument of world significance, St. Sophia in Kiev. "Lame" aesthetics formed a corresponding ethics one of whose victims became St. Sophia in Kiev. Being continuously destroyed physically in the Middle Ages by external enemies, in the 19th century it lost once and for all its artistic image, alas, through, in Tolstoy's words, the vandalism of the so-called restorers.

It so happened that the existence of ancient frescoes under the 18th century white painting became known during the reign of the patron of art Nickolas I. By all parameters, not only moral ones, it was the time exactly opposite to that when St. Sophia had been built: created as the spiritual and material centre of Prince Yaroslav's city, it began to be restored in the crisis period of the city as a whole. And restorers, following icon-painters, ceased to feel the energy that had inspired its creators. Ethical premises stemmed not from the study of the monument, but from purely speculative tasks characteristic of the dying academic art. Suffice it to say that Academician Fyodor Solntzev, put in charge of the restoration works by the Czar and the Metropolitan Philaret, permitted ancient frescoes to be cleaned from later white paint ... by unskilled labourers. Having stripped off (it cannot be termed otherwise) the plaster, Solntzev set as his "goal" the renewal of frescoes" /6/. The frescoes, revealed and finished disregarding the ancient fresco contour, coated with drying oil and resinous varnish, were not only spoiled, but sometimes iconographically had nothing in common with the originals. It is sufficient to name the fresco depicting the images of Prince Yaroslav's daughters which was turned into "Sophia, Vera, Nadezhda, Lyubov". From the first years of Soviet power St. Sophia remained one of the principal objects of protective activity of the People's Commissariat of Education, the Ukrainian Committee of the Protection of Ancient and Artistic Monuments, the Archeological Committee of the Ukrainian Academy of Sciences. At the time of the social upheaval of the young Soviet State its protective activity as if accumulated the entire cultural life of society. Academicians A.No-

vitzky, N. Makarenko, G. Lukomsky and V. Modzalevsky, the most prominent Ukrainian artists M. Boichuk and G. Narbut and restorers invited from Moscow, Petrograd and Pskov took part in the restoration of monuments of the "Mother of Russian cities", Kiev, and in the first place St. Sophia in Kiev. The ethical approach to the preservation of monuments changed radically. Art and ethical knowledge was now at a different level, but the most important was that the collective leadership in the political life of the country, allowing debates on the acute political subjects, was transposed to the ethics of science which substitutes an open concerned research activity for private solutions. Hence, not two high-ranking persons (as was the case in the 19th century), Nicholas I and the Metropolitan Philaret, now decided the fate of St. Sophia, but the most competent committee believing that "repairs should be confined to securing what was retained from the original frescoes, and in no case they should be completed by painting ... through a falsely construed restoration", and noting the negative result of the mid - 19th century restoration which "fully concealed the original appearance of the frescoes", "and in some spots just "destroyed" them /7/.

As shown further by this brief extract, the 1920s enriched theoretically and vastly the ethics of restoration and the approach to its very difficult problems.

Unfortunately, in the period of the famine and slow reconstruction of the devastated economy the results of practical restoration were substantially weaker. It seemed that far-reaching research could have been implemented back in the 1930s, but alas, "... Professor N., on his return from his trip for research purposes to Novgorod and Pskov, called on me and said that in Novgorod unreasonable restoration contradicting the archeological data was being undertaken of an ancient stonewall which it would spoil". In addition, "St. Lazarus Church dating to the same period (the 14th century - L.P.) and needing ordinary repairs only was pulled down, too. In Pskov they are now pulling down an ancient wall to be replaced by a new one in the pseudo-ancient taste (spacing is mine - L.P.). In Izborsk they are doing everything to disfigure an ancient wall with unnecessary annexes". "In Moscow they pulled down the ancient bell tower of the Strastnoy Monastery, and it collapsed onto the pavement like a felled tree so that not a single brick broke off, so strong was the brickwork, and in its stead a new pseudo-Russian bell tower was built. Same was the fate of the Yavlenny Nicholas Church in Arbat dating to the reign of Ivan the Terrible and built so strong that it was hardly possible to break one brick from another by using iron crowbars" /8/.

This quotation from Tolstoy's letter dated 1860 is in full accord with reports of monuments being destroyed in Moscow, Kiev and other ancient cities and towns of the USSR in the 1930s. The fate of art itself is repeated: the aggressive destruction of monuments of the past coincided with a no less aggressive rejection of the new, which is the result of the policy, similar in the two periods, based on the possibility of people having no idea of the elementary essentials of historical science and of elementary ethics as well, interfering with, and deciding upon, cultural matters. Tolstoy explained the destruction of monuments in the mid - 19th century by conservatism and inertness; distortion of great Leninist ideas of the protection of the people's magnificent heritage and the entire policy of building up a Socialist State is the explanation of the destruction of ancient and cultural monuments in the 1930s.

The castrated aesthetic program became also an ethical program. St. Sophia in Kiev "endured", although the question of its being pulled down was on the agenda. The ethical considerations "arose" thanks to the arrival in the Soviet Union of Romain Rolland who took interest in the portrayal in St. Sophia of Anna Regina, the wife of the French king Henry I and the daughter of Prince Yaroslav the Wise.

Unfortunately, he had no descendants in St. Michael's Gold-topped Cathedral which was, alas, considered outside the laws of historicism and just as the "richest, to quote the then press, source of easy money and a method of fooling the consciousness of the masses" /9/. In 1934 it was blown up.

Naturally, restoration at that time was thrown back to a mechanical level. Those ethical problems that were based on far-reaching art studies, determining an ethical approach to some or other method of restoring a specific monument, gave way to old-style work based on a personal initiative and personal ideas not governed by any ethical considerations. Restoration in the 1930s

did not enrich the painting image of St. Sophia either. Thus, in these years, as also in the years that followed the Decembrists' Uprising of 1825, Russian art lost its sources and its future, not for the first time vividly demonstrating the unfitness of the government's voluntarism exterminating the spiritual and ethical ideals of society. Spiritual values created in accordance with the laws of conscience were not needed. They reminded one of it and appealed to it both in Nicholas I's and Stalin's epoch. The art of the past lost its "historicism" and seemed squalid, and the present-day art seemed primitive and limited.

Therefore, when in the late 1950s Soviet study of art and aesthetics reconsidered "historical evaluations" of the art of the preceding period, restoration was facing the problem of its role in the rehabilitation of the true history of national art and the necessity of an ethical approach to all that had been bequeathed by the past generations: from the great to the minor. Restorers were confronted with the ethical necessity of taking into consideration the purpose of restoring each type of a work of art. We shall now turn to such "type" of national art which has been underestimated for decades, nearly forgotten and resurrected only now. The more so that the painting of this "third culture", as it was termed by researchers, was in the first half of the 19th century more "historic" than that of religion of which we spoke in connexion with the restoration of St. Sophia.

The fact that restorers turned to these works of art, and that they were in effect discovered as an entire stratum explains to a full extent how much the ethical norms of restoration have changed by now, the norms conditioned, repeat, by a different level of aesthetics. In the 19th century the city had a stratum created which had not tasted the "fruits of enlightenment", living in an old fashion and having its own artists, the former peasants bearers of living folklore traditions and who often produced outstanding professional masters. Directly dependent upon the modern level of the study of art, not only national, but also European, which has determined a new trend towards the cognition of artistic culture as a single whole in which all microstructures (from peasant to professional) are closely interdependent, the restorers' field of vision covered not only art as such, but also a broader concept - artistic life including forms and methods of the existence and functioning of art in society at its various levels.

The framework of the study of beauty were extended, and the contemporary restoration science was confronted with new tasks, simpler as compared to the restoration of masterpieces. The traditionalism and static nature of compositional and painting schemes enabled the restorer to interfere with the process of restoration more actively (but, repeat, now on the basis of knowledge and not speculation) than it was possible with works by outstanding painters.

The seeming simplicity of restoring works of art of second and third rate, however, proved in effect quite vulnerable. Relying upon elementary painting qualities it first seemed possible to complete and even re-paint them easily; an artist's personality and individuality was as if disregarded. And, repeat, it was only the development of the study of art and aesthetic thought that enabled the restorers to find a required ethical criterion. Therefore, the conservation and restoration of works of art of this kind is done by specialists on the basis of method premises appearing to be in the given case most fruitful. At the first stage they believed more essential, in the words of a prominent Soviet restoration theoretician, the late L.A. Lelekov, to see the woods as a whole than look at individual trees. The restorers saw in the course of their work that portraits and the merchant portrait were not identical notions, that the latter is distinguished by the integrity of its style, for it reflects the uniformity of social and aesthetic views of those who were painted and those who painted. They (restorers) abandoned the customary criteria of the academic regularity of a drawing, form modelling, line perspective and the like, and realized that they were facing art of a different level, with qualities and limitations characteristic of it alone, for this phenomenon is based on an aesthetic constant of another kind not determined by rigidly limited categories relating to professional art. Proceeding from this concept the restorers did not disturb, even when it was necessary to interfere very seriously with the restorative process, a true picture of the evolution of painting in the Russian provinces, which occupied an important place in the general picture of national art. Thus, in this case aesthetic principles correctly determined the ethical position of restoration, owing to which the study of art took in its fold a most

interesting layer of painting available for further research. What the restorers have done will make it possible to show how Russian urban culture started and advanced in the early and mid - 19th century. Finally, its boundaries determined from "below" (i.e., from folklore) by Gorodetz paintings, and from "above" (i.e., from cultivated amateur artists) by the phenomenon of Grigory Soroka, were completely filled. The aesthetic of provincial masters' creativity determined the ethics of the restorers, which enabled them to put works of art they had restored in a certain valuable line and perceive the history of Russian art not only in a radical change of styles, but also in a more plastic evolution. Thus, the experience of different periods in the history of national culture vividly shows that the ethical and aesthetic programs in restoration are invariably interdependent and reject alternative solutions.

Bibliography

1. A.K.Tolstoy. Collected Works, vol. 4, Moscow, 1964, p. 123.
2. N.N.Wrangel. Art and Czar Nickolas I. Old Years. 1913, May--July, p. 54.
3. A.K.Tolstoy. Ditto, p. 122.
4. A.K.Tolstoy. Ditto, p. 123.
5. A.K.Tolstoy. Ditto, p. 122.
6. L.I.Popova. The Historical Fate of the Fresco Painting of St. Sophia in Kiev. The manuscript approved by the Scientific Council of the Ukrainian SSR Academy of Architecture, 1950. (It is kept in the archives of the historico-architectural preserve "St.Sophia Museum").
7. The Kiev State Archives of the October Revolution, folio 166, p. 1, unit 215, sheets 29, 30.
8. A.K.Tolstoy. Ditto, pp. 121, 122.
9. F.Molchanivsky. Archeological Prospecting in the Territory of the Former St.Michael's Cathedral in Kiev. - The Proceedings of the Institute of the History of Material Culture, the Ukrainian Academy of Sciences. Book 2, Kiev, 1934, p. 123.

ABSTRACT

Founded in 1970, the Bolivian National Art Conservation Center began as a branch of the National Art Museum in La Paz and became part of the Bolivian Institute of Culture (IBC) in 1975. Technical assistance and supplies have come primarily from UNESCO. Teachers at the Center include an international list of visiting conservators, and Bolivian conservators and trainees have studied in Peru, Europe, and the U.S. Since 1978, the Center's projects have included two major 17th century colonial sites in the Andes, at Carabuco and Curahuara de Carangas, as well as work in Potosi and other colonial sites on paintings and murals. The Center currently has a staff of 10 and a modest but modern and well-equipped laboratory at the National Art Museum.

KEYWORDS

Bolivia, art conservation history, conservator training, international assistance, laboratory growth.

THE BOLIVIAN NATIONAL ART CONSERVATION CENTER Its History and Organization

Carlos Rua
Chief Conservator
Bolivian National
Art Conservation Center

Anton Rajer*
Visiting Conservator
1508 South 14 Street
Sheboygan, WI 53081

Introduction

Bolivia is particularly rich in Spanish colonial paintings and pre-hispanic artifacts. There are an estimated 25,000 paintings from the colonial period throughout the country, primarily in the national museums and in Bolivia's churches. Art conservation in Bolivia is characterized by large collections of cultural patrimony, primarily from the colonial period, and minimal resources to care for and conserve the collections. Throughout the entire nation there are at present no more than a dozen trained conservators and only one functioning laboratory, in La Paz. A number of foreign governments are supporting architectural restoration in Bolivia, but as yet no single grant agency has assisted in painting conservation treatments. Many proposals have been written outlining plans for the care of the cultural patrimony, but because of economic and political problems, most remain stalled. Despite these odds, progress has been made in the preservation and inventory of collections. A major step has been taken in the identification of collections and, with training and money, the number of labs carrying out treatments can be increased.

Since its founding in 1970 the Bolivian National Art Conservation Center in La Paz has played a key role in helping Bolivia to preserve its cultural heritage. The Center's role has been steadily expanding throughout the country, despite severe economic handicaps. With assistance from the international community, the Center has gradually progressed from a one-room, poorly equipped studio to a modest but modern facility with trained staff, adequate equipment, and large-scale conservation projects ongoing throughout the country.

Development of the National Art Conservation Center

Interest in the nation's artistic heritage began in the 1950s with the publication of books on Bolivian colonial art and architecture. In the 1960s it was suggested that courses in art conservation be introduced at the national university in La Paz. Unfortunately, San Andres University in La Paz was not equipped to undertake such a program, due to severe economic and political problems. In 1970, however, with assistance from the Bolivian Ministry of Education, the Sub-Secretary of Culture organized a small conservation facility at the National Art Museum. The studio was located in the National Museum because of the large and important collection of colonial paintings there in desperate need of care. The intention was to treat the paintings so that they might be placed on display, as many of them had come from remote colonial sites and villages in the Altiplano.

The museum director at that time, Mrs. Teresa Gisbert, supported the studio from the beginning and fought against great odds, such as lack of personnel and lack of funding, for its implementation and growth. The first studio was located in the museum attic and was equipped with a table, an easel, and a few brushes. The first staff person was a part-time volunteer. Spain and Mexico provided the first technical assistance for training, in the form of short courses.

In 1973, Bolivia participated in a meeting, organized by UNESCO in Lima, Peru, on the defense of cultural properties. This meeting was also attended by representatives of Peru, Ecuador, Columbia, Chile, and Venezuela. A joint document was sent by these six nations to UNESCO, requesting technical assistance to care for cultural properties.

In 1975, The Bolivian Institute of Culture (IBC) was established and included institutes devoted to archaeology, anthropology, literature and history, arts and music, visual art, and artistic cultural patrimony. At that time, the museum's art conservation department was renamed The National Art Conservation Center and was placed under the administration of the Institute for Cultural Patrimony, along with a national project to

* Author to whom correspondence should be addressed.

catalogue all institutional and religious collections through a central office in La Paz (See fig. 1).

This same year marked the arrival of the first donation to the Center of materials and supplies from UNESCO. This donation, valued at \$30,000, included a stereo microscope, a portable X-ray unit, linen, pigments, resin, and brushes. The large supply of new materials created the need for larger rooms to house the Center, and the conservation studio was moved from the attic to the first floor of the museum building. The UNESCO program of cooperation was complimented with technical assistance from foreign experts. Juan Corradini from Argentina was sent to the Center by UNESCO to teach introductory painting conservation courses in 1975 and 1977. Students for these courses were selected primarily from programs in the visual arts. The Center was required to send these newly trained conservators from La Paz to other Bolivian cities and villages with historic collections.

The Center's Conservation Projects

In addition to several large-scale conservation projects, the Center has concentrated its efforts thus far on the treatment of paintings on fabric from the colonial period. UNESCO and other organizations have occasionally sent conservation experts to teach mini-courses on the conservation of stone, paintings, mural painting, and polychromed wood.

The first large-scale project for the Conservation Center outside of La Paz was the emergency treatment of 17th century murals in Carabuco, on the shores of Lake Titicaca. This project was begun in 1978 with funds provided by UNESCO. The church at Carabuco is important artistically and historically in that the entire contents date from the 16th and 17th centuries, including a silver altar, four large (4m x 6m) paintings on fabric, and hundreds of square meters of murals painted on plaster on adobe. In 1980, UNESCO sent a Peruvian mural conservator to direct part of the work at Carabuco. Technicians were trained to consolidate the adobe and murals and to replace the reed and tile roof. The project has continued on and off for many years, depending upon funding. The Iberoamerican Institute for Cooperation (the cultural branch of the Spanish Embassy in Bolivia) and the West German Embassy in Bolivia were major supporters of the project.

The second major in-situ project to be undertaken by the Center was an emergency conservation effort at Curahuara de Carangas, near the Chilean border in the Andes. The church in Curahuara was built at the end of the 16th century and is made of adobe with a reed roof. The entire interior is covered with tempera frescoes that portray scenes from the Bible. The site is very remote and only accessible during the dry season. The actual conservation work began in 1984 and concentrated on consolidation only, as budget constraints did not allow restoration. West Germany was the major supporter of this project.

The projects at Carabuco and Curahuara de Carangas illustrate the enormous difficulties that the National Art Conservation Center has had to contend with over the years. These conservation sites are in remote, sparsely populated areas more than 12,000 feet above sea level. All supplies were transported in four-wheel drive jeeps, during periods when the dirt roads were passable. Both projects were suspended from time to time, due to economic constraints.

Potosi, the great colonial mining city that was recently declared International Cultural Patrimony by UNESCO, has also been the focus of the Conservation Center's efforts. Here most of the work has been carried out in numerous colonial churches. Assistance for these projects has been forthcoming from the OAS and the Spanish Embassy.

The Center has also undertaken projects in other cities: in Tarija, work is currently concentrated on the conservation of fabric mural paintings from the early 20th century in an art nouveau style home that has now been designated the Casa de la Cultura. In Callapa, Caquiviri, and Tiahuanacu, emergency conservation and structural stabilization of churches and art work was carried out by Conservation Center staff and local individuals.

Recent Developments and Future Prospects

In 1987 the Conservation Center sent its chief conservator to Mexico City to participate in a course for professionals in the field of painting conservation, co-sponsored by UNESCO/PNUD (the

regional United Nations development authority of South America) and the Getty Conservation Institute. In recent years, Bolivia has also sent a number of conservators abroad for schooling in Spain, Mexico, Peru, and Belgium, through international scholarships.

During the fall of 1987, a national seminar for professionals in museum administration, painting, and paper conservation was held in La Paz. The course was taught by American conservators, with support from Bolivian public institutions and private Bolivian and American industry. The seminar was repeated in 1988 and 1989, also with American participants. The outgrowth of this international effort has been the placement of Bolivian conservators and administrators in internships at American cultural institutions.

The National Art Conservation Center continues to be housed on the first floor of the National Art Museum in La Paz. Today it occupies about 1,000 square feet in three rooms. Two of the spaces are workrooms, and the third is used for materials storage. In recent years the Center has acquired a research microscope, an ultraviolet lamp, and two spot suction units. The Center now has a staff of five conservators and five technicians. All conservators and technicians work in the field as well as at the Center.

One serious problem for the Center is the difficulty of retaining staff, since salaries are very low. Another major difficulty is getting supplies, such as BEVA and Plextol, from abroad--a result of lack of funds and high domestic import tariffs. Despite these problems, significant accomplishments have been achieved at the Center: increased physical lab space within the National Art Museum building, continued progress in training at basic and advanced levels for staff, and the acquisition through donation of technical equipment and modern conservation supplies. It is hoped that a university course to teach conservation might be developed in Bolivia and that regional labs might be established throughout the country. The Center continues to work closely with other IBC departments devoted to the preservation of Bolivian cultural patrimony.

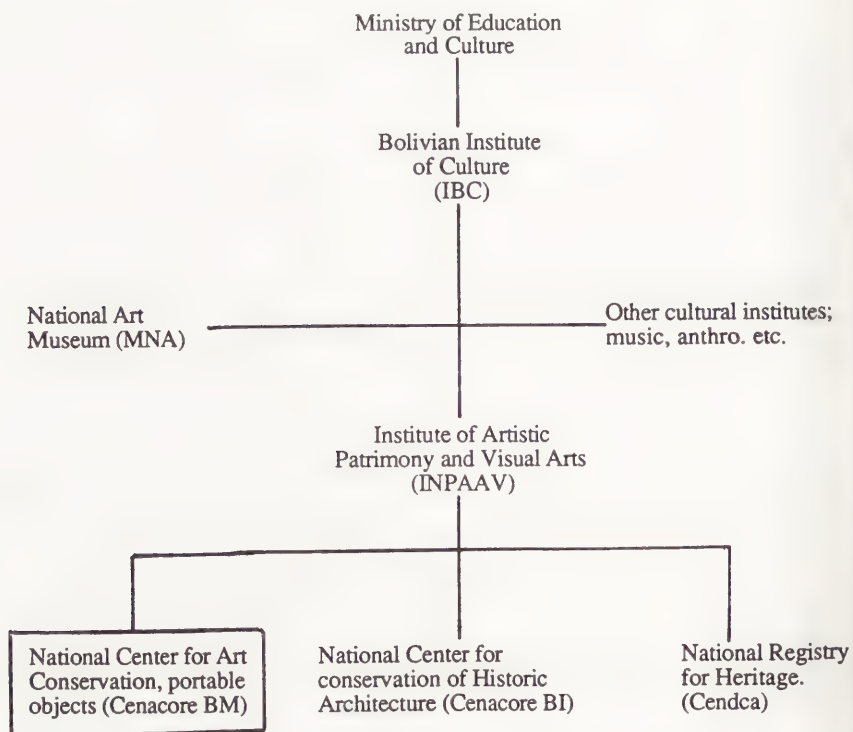


FIGURE 1. Organizational scheme of institutional art conservation in Bolivia.

ABSTRACT

The paper is devoted to the problem of protection of cultural and artistic heritage of the peoples of Central Asia in 1929-1941. Along with the achievement in propagating monuments of antiquity, their repairing and restoration, and growth of museums, connected in many ways with the spread of archaeological activity, the paper points out grave errors in the organization of protection and restoration of monuments on the threshold of the 20s-30s.

The experience in approaching the problem in Central Asia in the pre-war decade might contribute to the promotion of the system of protection and restoration of monuments in the USSR, as well as to the organization and development of the system of preservation of national heritage in other countries.

KEYWORDS

Cultural and artistic monuments, archaeological findings, protection, restoration, museum storage.

PROTECTION AND RESTORATION OF CULTURAL AND ARTISTIC MONUMENTS OF CENTRAL ASIA IN THE PRE-WAR DECADE (1929-1941).

B.Ya. Stavisky

Institut de recherches scientifiques pour la restauration
10, Krestyanskaya pl, VNIIR,
109172 Moscou,
URSS

As is known, Soviet Central Asian republics are extremely rich in old monuments. Prior to the Great October Socialist revolution there was no state legislation and no state bodies on protection and restoration of these monuments; and their preservation depended a lot on personal inclinations of some or other representative of the tsarist colonial administration. The establishment of a state system of protection and restoration of cultural and artistic heritage of Central Asian peoples has been one of the important achievements of Soviet power, and its publicizing, an account of successes, difficulties and errors in the development of this system may help not only us in its further organization of the cause of preservation of their national cultural monuments.

The first stage of the history of protection and restoration of cultural and artistic monuments of Soviet Central Asian republics is linked to the activities of the Turkestan Committee on Museum and Protection of Monuments of Antiquity, Art and Nature (Turkomstaris) and its successor the Central Asian Committee (Sredazkomstaris). The Turkomstaris was established in 1921 by the Government of the Turkestan Autonomous Soviet Socialist Republic (TASSR), set up after the October Revolution in Turkestan, as Central Asia was then known, and which was within the Russian Soviet Federative Socialist Republic (RSFSR). The Turkomstaris existed till 1925 when the existing national Uzbek, Turkmen, Tadzhik and Kirghiz Soviet Socialist Republics, full members of the Soviet Union (Uzbekistan and Turkmenistan received the status of union republics already when Tadzhikistan prior to 1929 was within the Uzbek SSR, Kirghizstan became a union republic in 1936) were established in lieu of the TASSR, and the Bukhara and Khiva Soviet People's Republics united with the RSFSR as a result of national demarcation in Central Asia. After the national state demarcation the Turkomstaris was reorganized into the Sredazkomstaris retaining a common Central Asian character.

Already before the Turkomstaris was established the TASSR Government of Soviet Russia, headed by V.I. Lenin, issued a number of decrees and enactments launching state legislation on protection of the cultural and artistic heritage of Central Asian peoples. The Turk- and Sredazkomstaris did a lot not only for the development of this legislation, but also for its practical implementation. Thus, workers of these Committees carried out work on finding, investigating and placing under state protection the most significant archaeological and architectural monuments in this region, executed repair and restoration works at some of them, guided the reorganization and expansion of four old museums, in Tashkent, Samarkand, Ashhabad and Fergana, and the establishment of new restoration of archaeological findings, in particular, the removal from the walls of a palace building, discovered during the Samarkand excavations, alabaster (stucco) panels and their preparation for a museum exposition. Of great significance for the activities of the Turk- and Sredazkomstaris was the elaboration by them of theoretical foundations of conservation and restoration of ancient monuments, including both architecture and museum valuables. The Turk- and Sredazkomstaris as a single common Central Asian organizational and scientific methodological center, established a close permanent contact with state and scientific institutions of Moscow and Petrograd (Leningrad), which participated directly in the work of these Committees ensuring a high level of these works and supporting the Turk- and later Sredazkomstaris with their scientific authority 1/.

After the national state demarcation in Central Asia it was proposed that in each republic its own Committee be established, which would work under the auspices of the Central Asian Committee. Economic and other problems, however, prevented the Sredazkomstaris from further development as center of the state protection system of Central Asian monuments, and the Sredazkomstaris itself ceased to exist in 1928. The winding-up of the Central Asian Committee, before in each republic conditions were created for the establishment of national institutions on the study and protection of monuments, was premature: this at

the start made difficult the setting up and activity of such (republican) institutions. The problem was that the financial position of Central Asian republics was far from easy, and expertise and personnel were simply lacking. In addition, at new, pre-war, stage the cause of the study and protection of monuments in each Central Asian republic went its own way, frequently differing from that of its neighbours /2/.

The most favourable, it would seem, were the conditions for the activity of the Uzbek Committee (Uzbekkomstaris), direct successor of the Sredazkomstaris, which inherited from it also all the experienced personnel for the study, protection and preservation of Central Asian ancient monuments. The Uzbekkomstaris was able, however, to launch its activities only a few years later; it was the result of a ministerial conflict, the fact that the Uzbekkomstaris, after the Uzbek SSR Government was removed to Tashkent, remained in the former capital of the republic, Samarkand; but, most important was the fact that some of the then leaders disregarded the necessity of a careful and sciencebased approach (as was the case with the Turk-and Sredazkomstaris) to the cause of monument preservation.

It should be emphasized, however, that even in these difficult conditions workers of the Uzbekkomstaris, in the first instance, of the former Samarkand commission, did what they could to continue their activity. Particularly noteworthy is the work on publicizing knowledge of ancient monuments of this old city. For this purpose in 1929 they, in particular, re-issued (first published in 1926 by the Sredazkomstaris) M.E.Masson's popular science booklets devoted to the most significant Samarkand monuments /3/. The greatest achievement in the cause of preserving Samarkand monuments was the straightening of the famous "falling minaret". This thirty-two-metre-high minaret flanks the magnificent facade of the oldest of the three structures in Registan (Samarkand central square), Ulugbek's Medresse (school), erected by Tamerlan's famous grandson in the 15th century. The inclination of the minaret caused panic among the city inhabitants back in autumn 1918. Then, to solve the problem of rescuing the minaret, a special commission was urgently established, headed by V.L.Vyatsky, a well-known Turkestan historian, the greatest authority on archaeology and protection of monuments in Central Asia in the pre-revolutionary period and the first fifteen years of Soviet power, later Chairman of the Samarkand Commission; The project worked out by architect M.F.Mauer, member of this commission, succeeded in preventing the minaret from falling down. To do so, the minaret in its middle was belted with a clapboard corset which was embraced with 24 steel ropes fixed to wooden anchors dug into the ground. The movement of the "falling minaret" was halted, although its upper part moved 1.8 mtrs away from the normal vertical position. Later the wooden anchors had to be changed or moved to new positions, but in general, the provisional system, created in 1931, for nearly one and a half decade delayed a further inclination of the minaret. And finally, in 1932, fixtures manufactured on a special order by the Moscow "Mosmet" Works, replacing the old devices, made it possible to straighten the minaret fully and relieve it of its wooden corset, stays and metal structures. Thus, for the first time in national restoration practice the 15th century minaret was rescued from destruction, a masterpiece of Central Asian architecture /4/. The experience of the rescue of this minaret was successfully made use of in the straightening in 1956 of another much inclined South-Eastern minaret of the same medresse.

That same year 1932 Uzbekkomstaris was moved to Tashkent and was able to become an institution on a republican scale, which is proved by the publication already in 1933 of a valuable series of booklets "Proceedings of the Uzbekkomstaris", issues 1, 2-3, 4 and 5 (1935-1936 saw the publication of 6-7th and 8th issues of this series). Like Turk- and Sredazkomstaris, the Uzbek Committee went actively into archaeological excavations in the territory of Uzbekistan and, partly, of other Central Asian Republics, as well as into museum construction.

Unlike the first stage of the history of protection and restoration of Central Asian monuments, the study and preservation of cultural and artistic heritage of Central Asian peoples in general, and monuments of Uzbekistan in particular, in the pre-war decade was conducted already not by one (as the Turkomstaris in 1921-1924, and Sredazkomstaris in 1925-1928), but by a number of agencies and institutions. The most important of them in the 1930's were the Uzbek SSR Committee of Sciences (just before the war it was transformed into the Uzbekistan Branch of the USSR Academy of Sciences) publishing, beginning from 1933, the journal

"Sotsialisticheskaya Nauka i Tekhnika", which carried materials of both the Uzbekkomstaris and Museum Department of the Uzbek SSR People's Education Commissariat.

Principal Factors contributing to the development of the study and preservation of Uzbekistan monuments in the 1930's were an expansion of archaeological investigations in the Republic and its museum network.

In the prospecting and digging works, which on an unprecedented scale were carried out by Soviet archaeologists from Moscow, Leningrad and Tashkent, were involved, apart from the Uzbekkomstaris and Uzbekistan Branch of the USSR Academy of Sciences, also the Arts Studies Institute of the Uzbekistan Committee of Arts, Central Asian State University (Central Asian Archaeology Department was opened in it in 1940), Central Asian Industrial Institute and individual museums of the Republic. As a result of these works (they were on a particularly large scale in the middle - second half of the 1930's) numerous monuments of ancient civilizations were discovered in Uzbekistan, which had never been heard of, and very rich materials were obtained, which substantially added to museum collections of the Republic and partly Moscow and Leningrad museums. And this, certainly, contributed to a more profound study of both archaeological and architectural monuments and museum valuables, and problems of their preservation and restoration. The 1930's were the beginning of a quite new type of archaeological investigations, most closely linked to the study and protection of ancient monuments: archaeological supervision of large construction sites; The most significant of such construction site expeditions in the 1930's in Uzbekistan (and Central Asia as a whole) conducted in 1939 an investigation of archaeological monuments and collection of individual findings in the construction zone of the Grand Fergana Canal which was 267 km in length /5/. After WWII such expeditions became an ordinary event in Central Asian republics and the entire Soviet Union; They are financed, in conformity with the USSR Council of Ministers Decree, out of the budget allocations planned for these large construction projects.

As was already noted, further development of the Uzbekistan state museum network occurred in this decade. True, at the start of this period certain damage to museum development was done by erroneous directives of the 1st USSR Museum Congress, 1930 denigrating the significance of authentic museum materials in the exposition. In time this mistake was corrected, however, and the enhanced role of museum in scientific and educational work and the appearance of a large number of new archaeological, numismatic, artistic and other additions to museum stores contributed to the development of existing and establishment of new museums (by the beginning of WWII the Republic had over a dozen and a half of them, in so doing, apart from Tashkent, Samarkand, Bukhara, Khiva, Kokand, Fergana and Namangan state museum were opened in the 1929-1930's also in the then capital of the Karakalpak ASSR Turtkul, in Termez, Karshi and other Uzbekistani cities and towns).

Practical conservation and restoration works at architectural monuments, conservation and restoration of archaeological findings and other museum valuables were also on a large scale in this decade. We already spoke of the rescue of the "falling minaret" of the Uluzbek Medresse in Samarkand in 1932. At that time and in the following years repairs at some other monuments were also carried out. Among restoration works in the 1930's one should mention the restoration of the wonder of the 9-10th century architecture, the Samanids' Tomb in Bukhara. The complete restoration of this tomb carried out in 1937-1939 under the guidance of well-known historian of architecture B.N. Zasyarkin and with the participation of Uzbek master Usto Shirin Muradov is estimated as one of the best examples of the restoration of the original appearance of the ancient building /6/.

The training of scientific (historians, archaeologists and ethnographers) and museum specialists played an important role in the improvement of investigation, protection and restoration of Uzbekistan monuments in the decade under consideration.

The experienced, but few in number, workers of the Turk- and Sredazkomstaris, who laid down the foundation of the preservation system of Central Asian monuments, including those of the Uzbek SSR were not sufficient; moreover, not all of them were living by the time archaeological, restoration and museum works were conducted on a large scale (V.L. Vyatkin, for example, died in 1932; Academician V.V. Bartold, a recognized leader of historical and archaeological investigations of Central Asia, permanent ad-

viser to all scientific societies and organizations of Turkestan and, later, Central Asia, great national historical orientalist, professor of Petrograd - Leningrad University, died a year before; the first head of the Turk-and Spedazkomstaris D.I.Nechkin died five years later). New scientific specialists were trained both in Uzbekistan itself - in the oldest higher educational institution of Central Asia, Central Asian State University, set up on V.I.Lenin's initiative, and in institutes of education established in mid-30's in Andizhan, Bukhara, Samarkand, Tashkent and Fergana, and in Moscow and Leningrad. Museum specialists were also trained extensively in the same period. Nine months refresher courses for museum workers were opened in 1929 at the country's central higher educational establishment by the decision of the RSFSR People's Education Commissariat. Special departments of museum-local lore character were set up in 1932 at Moscow, Leningrad and Kazan Universities; and Higher Museum Courses were opened in 1934. Representatives from national republics including Uzbekistan were trained at these courses and departments. In addition, museum personnel were trained on the basis of Tashkent and Samarkand Republican Museums. As a result by the time Nazi Germany attacked the USSR there were over 300 museum specialists in Uzbekistan.

Prof. M.E.Masson, a well-known archaeologist and Central Asian monument protection activist, whose works I repeatedly cited when characterizing the situation in Central Asia after the premature winding-up of the Sredazkomstaris, wrote: "It was worse in other (apart from Uzbekistan - B.S.) Central Asian republics were slowly formed Komstarises were at best fully formed by 1932. Newly appearing scientific organizations in these republics ... did research work apart from one another, and some contact was maintained individually by some workers" /7/. In these republics by mid-30's however, the situation began to improve. Along with Republican Komstarises, or their substitutes, there appeared also other scientific research institutions, Committees of Sciences, bases and branches of the USSR Academy of Sciences. And though archaeological investigations in Kirghizia, Turkmenia and, particularly, in Tadzhikistan in the 30's did not achieve such a scale as in Uzbekistan (archaeological works in all these republics reached large scale only in post-war decades), archaeological findings and materials became a factor there too, contributing to the development of monument protection and museum work; Practical repair and restoration works were also done in these republics on a much more modest scale than in Uzbekistan. Among these works there were, however, quite considerable ones, like, for instance, an archaeological and architectural investigation, for the purpose of restoration, of old Merv monuments and, first and foremost, Sultan Sanjar's famous tomb (first half of the 12th century), carried out in 1938 by Leningrad architects N.M.Bachinsky and V.I.Pilyavsky on the invitation of the Turmen scientific research institute of history /8/.

Museums and museum storage were improved in those years also in Kirghizia and Turkmenia, as in Uzbekistan. In Tadzhikistan, the only republic in the Soviet Union which did not have a single museum by the early 30's, in 1931 Khodzhen (now Leninabad) Museum was opened, and in 1934, the Republican Museum of the Tadzhik SSR in the capital of the republic /9/.

A more uniform legislation on the study and protection of monuments was developed in all the republics of Central Asia.

Conclusion

On the whole, the trend of development of preservation of cultural and artistic heritage was common for all the Soviet Central Asian republics in the pre-war decade. Having recovered somewhat from the errors committed in the late 20's and early 30's, the Central Asian republics established their own national bodies for the study, protection and restoration of cultural and artistic monuments, conducted works on the maintenance, and in some cases also scientific restoration of architectural monuments, improved (or set up, as was the case in the Tadzhik SSR) their own museums and museum activities, strengthened legislation on the preservation of their historical and cultural heritage and trained specialists required for the study and protection of monuments and for museum work. At this time scientific contacts of Central Asian institutions responsible for the study, protection and restoration of old monuments were strengthened again with scientific institutions of Moscow and Leningrad.

The 1929-1940 achievements in the study, protection and restoration of monuments in Central Asia lay in the foundation of a new

stage of developing the investigation and preservation of cultural and artistic monuments of Central Asian peoples, which began after the end of the Second World War and the restoration of the economy of the Soviet Union damaged by this war.

Notes

- 1/ See the details: B.Ya.Stavisky. Protection and restoration of cultural and artistic monuments of Central Asia in the first years of Soviet power (1917-1924) - ICOM Committee for Conservation. 5th Triennial Meeting. Zagreb, 1978 (78/ii/3), pp. 1-9; "The first steps of state monument protection and restoration system in Central Asia" by B.Ya.Stavisky and N.N.Zhukova in the journal "Iskusstvo" (Art), 1981, N°4, pp. 53-56; "On the history of the Establishment of the Turkomstaris" by the same authors in the journal "Obshchestvennye Nauki" (Social sciences) in Uzbekistan", 1981, N°3, pp. 51-53; "Protection and restoration of Central Asian cultural and artistic monuments" by L.A.Lelekov and B.Ya.Stavisky in the book "restoration of museum valuables in the USSR". Moscow, 1982, pp.157-167; "Conditions of cultural and artistic monument protection and restoration in Central Asia in 1925-1928" by B.Ya.Stavisky in the collected works "Artistic heritage. Storage. Investigation. Restoration". Moscow, 1983, vol. 8 (38), pp. 23-36
- 2/ The significance of this stage in the history of protection and restoration of Central Asian monuments has found little expression in scientific literature. For principal information on it, see "A short essay on the history of the archaeological study of Central Asia" (Part 1) by M.E.Masson. The proceedings of the Central Asian State university. New series, issue LXXXI, Tashkent, 1956, pp. 24-34; "Museum work in Uzbekistan" by N.S.Sadykova. Tashkent, 1975, pp.100-177.
- 3/ "Tamerlan's City Mosque known as Bibi-khanym" by M.E.Masson. Samarkand, 1929; "Gur-emir tomb, the Timurides burial vault" also by M.E.Masson; "Registan and its medresse" by the same author. Samarkand, 1929; "Samarkand tour guide" by the same author. Tashkent-Samarkand, 1929.
- 4/ The epic story of rescuing the north-eastern minaret of the Ulugbek Medresse in Samarkand is most fully and vividly depicted in M.E.Masson's booklet "The Falling minaret (from reminiscences of a participant in the support and straightening of the 'Falling minaret', 1918-1932)". Tashkent, 1968.
- 5/ In addition to short information reports, see a thrilling story of this expedition in M.E.Masson's book "From reminiscences of a Central Asian archaeologist". Tashkent, 1976, pp. 88-175.
- 6/ "The Samanides' tomb, an architectural wonder of Central Asia" by M.S.Bulatov. Tashkent, 1976, p.17. This work contains previously unpublished materials, including a detailed photo depiction, a measuring sketch of the Tomb and restoration works diaries.
- 7/ "A short history of Central Asian studies..." by M.E.Masson p.25.
- 8/ "A story of Sultan Sanjar's Tomb study and restoration" by N.A.Khan.- Information bulletin of the International Association on the study of Central Asian cultures. Ussue 7, Moscow, 1984, p.100.
- 9/ "The development of museum work in Tadzhikistan" by B.Ya.Stavisky, A.I.Manyakhina and E.Yu.Negmatullayeva in the journal "Iskusstvo" (Arts), 1983, N°1, pp. 51-55.

ABSTRACT

The paper considers various methods of restoration completion of sculpture. Proceeding from practical results, it suggests new methods of justified completion using casts off identical fragments of the same author's sculptures (developing Giovanni Morelli's attribution method).

KEYWORDS

Museum sculpture, restoration completions portrait, analogy, fragment, original.

METHODS ASPECTS OF RESTORATION COMPLETIONS

O.V.YAKHONT
10 Krestyanskaya Pl., Moscow
VNIIR
U.S.S.R.

Introduction

At the turn of the century a rule began to be established demanding the exclusion from museum and restoration practice scientifically unjustified completions, distortions and re-making of original sculpture (particularly of an ancient origin), which was commonly done in the past centuries /1/. With respect to restoration of ancient and medieval sculpture new requirements met with substantial recognition, although discussions sometimes occur of the results of the conservation of certain specific antique monuments (Apollo of Belvedere, Laocöon, Sleeping Faun from Munich, etc.) /2/. As far as restoration of the 17-20th century sculpture is concerned, it is carried out in different ways: sometimes (like antique sculpture) losses completion operations are excluded, which was marked on some classical works: J.A.Goudon's early works, A.Canova's and B.Thorvaldsen's sculptures, etc.; more often restoration operations are done according to the traditions of previous centuries - free, qualitatively unlimited completion performed intuitively (by feeling and guess work) whose result depends on the executor's experience and creative capacity. At the same time there can be observed a desire to meet contemporary scientific requirements: the use of documentary and visual (graphic and the like) justifications of fragments completed. Unfortunately graphic (flat, two-dimensional) images cannot fully restrict a subjective interpretation in making a three-dimensional fragment to be completed, that is, although they give an idea of the lost fragment, its three-dimensional execution, the quality of its surface, texture and other artistic aspects will depend on the restorer's (just like the sculptor's) creative capabilities.

Proceeding from contemporary scientific requirements and seeking to avert any subjective interpretation, we have been carrying out losses completion works (for the past two decades) only on the basis of an identical sculpture, a three-dimensional analogue /3/. The completion process itself is, to a certain extent, of a mechanical, and not of artistic interpretation nature, and constitutes the casting of the lost fragment, taken off a similar sculpture, with a subsequent completion in conformity with it (casts made of simulating material, etc.). The application of these methods is particularly necessary when restoring sculpture with a clearly expressed subjective nature of executing the form and texture (impressionist, modern, etc. sculpture).

In museum practice one has very often come across the necessity of restoring sculpture that has no identical repetitions (three-dimensional analogues). While carrying out restoration of the sculpture collection of the State Historical Museum for the last three years, we were confronted by a similar situation. This collection, containing several hundreds of works of different materials, has failed to attract the attention of specialists for many years, and has not been identified in real terms: it was unknown who was sculpted and who the authors were. In the course of conservation and restoration work we succeeded in attributing many of them and finding that there were sculptures in it, some of which were created by A.Canova, J.-A.Goudon, F.Leconte, A.-M.Collo, Ch.-D.Rauch, G.Goethe, F.Shubin, I.Martos, M.Antokolsky and other wellknown West-European and Russian sculptors. It turned out that there was a series of marble portraits of Napoleon I's relatives, executed by A.Canova who was commissioned by the emperor and stayed with him in Elba. Many of the collection sculptures depict prominent historical figures, but we failed to identify who some of the sculptures portrayed. Some of these sculptured portraits have though negligible, but fairly distorting losses which (in the opinion of museum exposition workers) make them hardly suitable for viewing in museum show-rooms. For instance, a tip of the nose was lost in the sculptured portrait of a military officer, which had the signature of F.Shubin, a leading Russian sculptor of the 18th century. This gave rise to the problem of its restoration, since this sculpture has a paramount artistic value for the Museum collection. When analysing the works by, and creative activity of, this sculptor, we believed it justified to complete the loss in the sculpture by resorting to the above-described methods extending their limits. In so doing we considered as fruit-

ful the ideas of Jovanni Morelli's (Ivan Lermolieff's) methods suggested over a hundred years ago for the attribution of old paintings /4/.

J. Morelli' noted rightly that, when depicting a human figure in the picture, the artist pays unequal attention to its different parts. The composition, pose, motion, face, eyes and mouth are of great significance in conveying the content of a work of art. That is why the artist gives them more creative effort. At the same time some parts are of lesser significance (the form and structure of a hand), and others are of no significance at all (ears, nails, feet, etc.). And yet the drawing and nature of the structure of these 'secondary' parts are fairly complicated, but artists in their execution resorted, roughly speaking, to well-learned and practiced (standard) methods and customary patterns (i.e., executing them to a certain extent mechanically uniformly). J. Morelli concludes from this that since each artist has his own practiced type of hand and ear, their structure and form may serve as a reliable determinant of the author of work of art.

Although J. Morelli's method cannot be universal (this has been proved by a hundred-year-long practice of attribution), it contains fairly fruitful ideas for restoration, too. In the sphere of sculpture, in the practice of its execution, one can find a great deal of additional examples of the sculptor's uniform execution of the form of an eye, the pupil of an eye, dripstone, ear pattern, its helix, nostrils and the form of the nose tip, carving hair, lace, fabric, its texture and some other details, the quality and manner of their execution.

In order to come to these conclusions we made several series of casts off similar fragments of a large groups of sculptures by some sculptors (eyes, eyebrows, nose tip, nose base, nostrils, ears, lips, etc.). In so doing we selected sculptures undisputably executed by them, and not their disciples or assistants. The stable manner, methods and character of using tools could be observed in the casts exceptionally clearly (from the general execution of form to the development of details, from the choice of tools in each case to the manner of their use). At the same time some of the sculptors, by virtue of their creative nature and external influence (trips to other countries: Italy, France where sculpturing has its own traditions) display some, though negligible, evolutionary changes in the technique and manner of executing certain details. But most often sculptures, executed with a ten to fifteen year interval, were nearly fully identical by the manner, methods and character of executing these details. This could be more vividly observed in sculptures of a classicism character (18th - first half of 19th centuries).

The reason for each sculptor's uniform execution of certain (most often secondary) details is that sculpturing is a very painstaking job compelling a certain unification of methods and using in these cases special and uniform tools. In addition, sculpturing has most stable age-old traditions which are manifested both in the nature of the art itself, and in each sculptor's work.

The result of this (a combination of traditions and individual execution) is peculiarly expressed in the manner and quality of executing the general form of sculpture and its details. That is why, by the analysis of sculpturing, one can obtain considerable information significant for revealing the author and history of a monument, reasons for degradation, tasks of restoration and subsequent preservation of sculpture.

Incidentally, when analysing the results of losses being completed by some restorers, we made a rather curious observation (which in a way led to the idea of this paper): restorer sculptors, completing noses, ears, fingers (and other details) not by a three-dimensional analogue, but by intuition and imagination, re-created in them to a certain extent their own features. The same was already in the past (beginning with Leonardo da Vinci's notes) defined as one of the characteristics features of artists' work. A similar thing can be observed in the works by sculptors executing the portraits of statesmen, imagined historical or canonized portraits. In these portrayals, when emphasizing the most characteristic, traditionally recognizable, face features and details (mustache, beard, head dressing and pose, etc.) one could observe secondary features and details revealing the author of the work (the pattern and form of the ears, nostrils, execution of the eyes and other parts of the face). It seems evident that such a phenomenon lies biologically in the nature of an artist having his own ideally shaped type of a face and its individual features.

Proceeding from the above-said we believe that, in solving the problem of completing some lost detail or some relatively secondary fragment, the restorer may use casts of similar details off the same author's work (with their appropriate adjustment for this particular work and its part). We prepared a series of casts of noses and their fragments off a group of sculptured portraits executed in the years nearest to F.Shubin's bust of a military officer to be restored. Although they portrayed different faces (the portraits of Catherine the Great, Z.G.Chernyshov, P.A.Rumyantzev-Zadunaisky, P.G.Chernyshov, A.P.Sheremetieva, B.P.Sheremetiev, P.B.Sheremetiev, V.A.Sheremetieva, etc.), the character of plastic execution of the eyes and the tip of the nose (and in some of them a considerable part of the nose) was so close (nearly identical) that the restoration council experts had no doubt as to the correctness of the suggested methods. A model was made on the basis of these casts, which, after having been approved by the board of experts, was executed in marble and fixed to the spot by means of a paste simulating marble /5/. Although the completion was made unnoticeable visually, its place and form can be determined by means of special equipment (X-ray, ultraviolet and infra-red rays), and it can be removed if necessary (by solving the simulating polymer paste).

The suggested methods cannot be universal and their application must be fairly sufficiently justified: they were used to restore a part of the sculpture fragment negligible in size (although its loss made the work unsuitable for the exposition). Therefore, the principal conditions must be the scientific justification of all operations and the reversibility of restoration completions (i.e., removal of a completed fragment safely for the monument).

Bibliography

1. O.Yakhont. Quelques extraits de l'histoire de formation des principes de restauration de la sculpture. - Third International Restorer Seminar. Budapest, 1988, pp. 242-248.
2. O.Yakhont. About Some Actual Problems of Restoration of Sculpture in Stone. - ICOM Committee for Conservation 5th Triennial Meeting. Zagreb, 1978 (78/10/7).
- W.Oechelin. Il Laconte - odel restaure delle status antiche. - Parogone, 1974, № 287, pp. 3-29.
- P.Jürgen. Antikongätzung und Entrestaurierung. - Kunstchronik, 1972, № 4, S. 85-112.
3. O.Yakhont. On the Restoration Methods of Museum Stone Sculpture. - Second International Restorer Seminar. Budapest, 1979, pp. 87-94.
4. I.Lermolieff. Künstlerische Studien über italienische Malerei. Die Galerien Borghese und Doria - Pamfili in Rom. - Leipzig, 1890, p. IX.
5. O.Yakhont. On the Restoration Methods of Museum Stone Sculpture. - Second International Restorer Seminar. Budapest, 1979, pp. 87-94.
- O.Yakhont. Several Notes on the Completion of Alabaster Works of Art. - Fourth International Restorer Seminar. Budapest, 1984, v. 1, pp. 242-246.

Working Group 12

Care of Works of Art in Transit

Protection des oeuvres d'art pendant
le transport



ABSTRACT

Little research has been undertaken on transportation of works of art by sea with publication of the results of monitoring the environmental conditions actually experienced. Two large tapestry cartoons by François Boucher were shipped from London to Muizenberg in an insulated container, May-June 1989, as deck cargo with the environmental conditions within both the container and the 'envelope' of the packing case continuously recorded. Although the external temperatures varied from 5°C to 31°C in the tropics the relative humidity of the air space containing the paintings changed slowly from 9% to 75% over the 13 days of the voyage. Such stable conditions are rarely achieved by other modes of transportation.

KEYWORDS

transportation, painting, container, sea

THE TRANSPORTATION BY SEA FROM SOUTHAMPTON TO CAPE TOWN OF OIL PAINTINGS IN A CONTAINER WITH ENVIRONMENTAL MONITORING

Peter Cannon-Brookes
Thrupp House
Abingdon
Oxon, OX14 3NE
United Kingdom

Introduction

Shipment of environmentally sensitive works of art long distances by sea, notwithstanding the enormous financial economies which can thereby be achieved, remains exceptional, and this mode of transport is usually chosen as a last resort. For many years the main objection to marine transportation was the combination of ad valorem freight charges wharfage charged for high value works of art which more than cancelled out the other economies to be gained. The ad valorem freight rates have now generally been abandoned, whilst vast improvements in the design, construction and operation of standard insulated containers encourage careful consideration of their use and marine transportation as an economic alternative to air freight, at least for outsize items or large consignments. Meanwhile little has been published concerning transportation of works of art by sea and few accounts of the practical experience which has been gained have been backed by precise measurements. The present paper is a modest contribution towards a better understanding of the environmental conditions actually experienced by works of art when containerised and transported by sea through the tropics.

Nathan Stolow (N. Stolow, Conservation and Exhibitions (London: Butterworths, 1987), 184-188) has discussed transportation by ship, though not the use of insulated containers, and more recent than the examples cited by him was the transportation of the Labia paintings in the air-conditioned mail room of R.M.S. Windsor Castle (P. Cannon-Brookes, "Transportation of a Consignment of Paintings from Cape Town to Southampton by Sea, September 1977", ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978, Paris: ICOM, 1978, 78/12/2/1-5). This was the last voyage of R.M.S. Windsor Castle, and although mail rooms are now generally a thing of the past, air-conditioned cabins on suitable ships provide good environmental conditions for the transport of small exhibitions. This technique was employed for the touring exhibition, Michael Ayrton, shown in Southern Africa in 1981-82 when the works were transported in light boxes in spare officers' cabins (Southampton - Port Elisabeth, 1981; Cape Town - Southampton, 1982). For the touring exhibition, The British Neo-Romantics, shown in 1982-83, insulated containers were used successfully (Southampton - Port Elisabeth, 1982; Cape Town - Southampton, 1983) but with the works packed in heavy insulated cases originally made for use by the Tate Gallery and without any environmental monitoring instruments.

Boucher Tapestry Cartoons

Count N.A.D. Labia has donated the house built by his father, Prince Natale Labia, at Muizenberg, between Cape Town and Simonstown, to the South African National Gallery, together with much of its original furniture and a number of paintings from the J.B. Robinson Collection. The new museum opened to the public in 1988 and for the ballroom Count Labia subsequently donated the two large tapestry cartoons by François Boucher which had been until 1987 on loan to the National Museum of Wales in Cardiff. Painted in oil on canvas during the mid-1750s for use at the Beauvais Manufactory, these had been cut up into small sections as a preliminary to basse lisse tapestry weaving and they were, towards the middle of the nineteenth century, reassembled into large decorative paintings, like the even larger pair of Boucher tapestry cartoons in the J. Paul Getty Museum, Malibu, which are en suite. The irregular sections of the original cartoons, together with replacements for any missing pieces and the enlargements to the compositions top and bottom, had then been assembled in new lining canvases, and although both paintings are in stable condition, their composite structure and size (3.15 x 1.83m, excluding frames) encouraged particular care in their transportation from Christies' warehouse in London to the Natale Labia Museum.

The Evolution and Application of a Transportation Strategy

A packing case of adequate size for the Boucher Cartoons, travelling on edge, can as airfreight only be carried as main



Fig. 1: Interior of the insulated container with the packing case containing the Boucher tapestry cartoons, after loading onto the deck of S.A. Sederberg. The box attached to the packing case contains the thermohygrograph recording the environmental conditions within the 'envelope' enclosing the paintings, whilst that on top records the conditions within the container itself.



Fig. 2: Insulated container after closure, surrounded on both sides and above by other containers so as to minimise solar heating.

deck cargo in a Boeing 747 or an aircraft of similar size. But between London and Cape Town such main deck airfreight facilities are not currently available and to take advantage of the Luft-hansa main deck airfreight facilities available between Frankfurt-am-Main and Johannesburg the paintings would have to be transported from London to Frankfurt by road and ferry, and from Johannesburg to Cape Town by road or by rail. Consequently a sponsorship deal was struck with the shipping line, Safmarine, and a standard insulated 20ft container was made available for the shipment at a special rate. The packing case for the pair of paintings was constructed by MoMart Limited of London, to specifications provided by the author, and the container was fitted out and loaded at MoMart's London depot. However, owing to the space taken up within it by the insulation and the fixed slatted flooring, the very large packing case required for the paintings could not be carried in the vertical position originally specified - only held at a steep angle - but on balance it was judged preferable to modify the original specifications and pack accordingly, rather than use an uninsulated container. The packing specification within the timber framed case was for a lining of heavy duty polythene sheeting taped together and held in position by sheets of 50mm expanded polystyrene, lined in turn with 25mm plastazote foam and an additional 25mm thickness on riding edges. These lining materials were extended through a porthole, 300mm x 150mm, in the vertical edge of the case facing the container's doors, and over all the interior of the box attached to it (see fig. 1). By this means, the interior of the box communicated directly with that of the packing case to which it was attached and a thermohygrograph installed within it, its sensor cage protruding into the airspace of the case, shares the same environmental conditions as the interior of the latter.

The packing and transportation strategy, since by definition the case was to remain at sea level throughout the voyage from Southampton to Cape Town, was that leakage of air in and out of the sealed 'envelope' provided by the polythene sheeting would be minimal, with the rate of temperature change slowed down substantially by the insulation layers in both the case and the container, and that more than adequate dunnage would be provided by the wood of the frames and the painting stretchers when the amount of free air within the 'envelope' had been minimised. Furthermore, it was agreed in advance that the container, with minimal delay at the dockside, would be stowed on deck level immediately forward of the accommodation and bridge. The container was also, by prior arrangement, to be stowed close to the centre line of the ship, with containers to each side and above so that only its end doors were exposed (see fig. 2). However, the gap between the stacked containers and the accommodation on S.A. Sederberg is barely 3m, and thus the only direct sunlight able to penetrate to the container is for a limited time twice daily, and then at a sharply oblique angle. It was subsequently learnt that this container position is that normally selected for shipping valuable horses and cattle, with the heating problems created by solar radiation reduced to a minimum. The insulated container, before the packed case was stowed within it, was carefully checked for evidence of any past leaks through its roof or sides, but as an additional precaution in the event of a new leak developing, a tent of polythene sheeting was erected within the container and over the top of the framework restraining the case.

On S.A. Sederberg the alternative would have been to load the container into one of the holds and seek to control the environmental conditions within the 'envelope' of the case by linking the container to the forced air supply duct serviced by the ship's refrigeration/ventilation system. So long as such a container could be the sole occupant of one stack in a hold, or share that stack with other containers requiring temperature conditions acceptable for it, closely controlled temperatures below 17°C can be provided, but access to the container is impossible once it has been lowered into the hold and any recording instruments provided must be sufficiently robust to withstand any small shocks registered during the loading process. For an escorted consignment deck loading is preferable since the recording instruments can then be set up after loading - and their correct operation checked before departure. Soon after the container was placed in position on the hatch covers of S.A. Sederberg, 22 May 1989, two Isuzu JS 25-00 thermohygrographs with new batteries and set to 31 days were installed by the present author as escort, one within the sealed box and thus the 'envelope' containing the paintings, and the other on top of that box, standing on a block of plastazote foam with another on top and the whole tied down by strings passing under the box. These two thermohygrographs had been carried onto the ship by hand and were only placed in position

when the risk of accidental jarring had become negligible. Even with special handling facilities, different, much more robust recording instruments would be essential for installation before loading on deck, or into the hold, if their reliable operation throughout the ensuing voyage was to be reasonably certain. Such equipment is, of course, freely available, but they are several times more costly than standard thermohygrographs and this is a significant economic factor in evolving a transportation strategy which could include shipping by sea. In respect of this particular shipment standard thermohygrographs were a welcome addition to the technical equipment of the new museum, whilst it had little use for more specialised packing case monitoring equipment.

Environmental Conditions Monitored

S.A. Sederberg sailed from Southampton on the midday tide of Monday 22 May 1989 and, without putting into port throughout the voyage, entered Table Bay, Cape Town, during the afternoon of Sunday 4 June. No rough weather was experienced and although the exterior gaskets of the container doors were checked twice daily throughout the voyage those doors were not opened from the time the thermohygrographs were placed in position on the morning of 22 May until shortly before unloading early in the evening of 4 June. However, the keys to the security locks were in the possession of the escort throughout and in the event of any untoward incident access could have been obtained quickly at any time. The ambient temperature conditions rose from around 15°C in Southampton to around 31°C in the tropics before dropping back to around 13°C in Cape Town on arrival (see fig. 3), with ambient relative humidity varying between 64% and 100% (see fig. 4).

Within the container the temperature range was between 15.5°C and 27.5°C, with the ambient relative humidity, after the first few hours, between 78% and 85%. The exterior of the packing case had been painted with an oil based paint and the lining of the container was made of resin-bonded fibreglass, and thus the dunnage within the large free air space was limited to the timber of the supporting frame. On the other hand, the conditions recorded within the container could not but be influenced by the very high humidity experienced in Southampton docks when the instruments were installed and the container doors closed for the voyage. The temperature recorded within the insulated 'envelope' of the case followed that of the interior of the container closely, with a 12-18 hour time lag, but the slowness of the changes in temperature were reflected in very stable relative humidity and a slow decline from 79% to 75% over 13 days. The undesirably high relative humidity level established within the 'envelope' before the instrumentation was installed is a reflection of the environmental conditions under which the paintings had been stored for the previous 18 months in London, but at least consistency had been achieved throughout the transportation process!

Conclusions

The very substantial economies which may be obtained by using insulated containers and transport by sea can be achieved without any loss of environmental control, and in shipping two large Boucher oil paintings from London to Muizenberg in May-June 1989 by this means, the environmental conditions achieved throughout the sea voyage were almost certainly a great deal more stable than those which would have been experienced using a simple packing case alone and the much more expensive combination of road, ferry and airfreight via Frankfurt and Johannesburg, notwithstanding the unsuspected initial high moisture content of these paintings and their frames which were responsible for the very high relative humidity within the 'envelope' for the duration of the journey. Furthermore, the total handling of the cased works was reduced greatly and an additional level of protection against both thermal changes and mechanical shocks was provided throughout the transportation process. Additional carefully monitored consignments of works of art transported by sea are needed for analysis, in particular with respect to the North Atlantic route, before more general conclusions can be drawn.

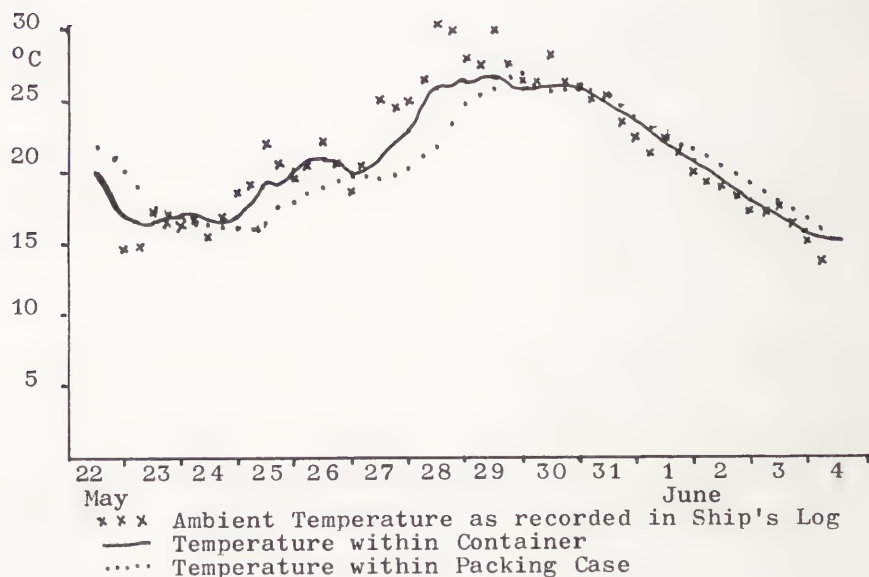


Fig. 3: Ambient Temperatures and those recorded within the Container and the Packing Case, 22 May - 4 June 1989.

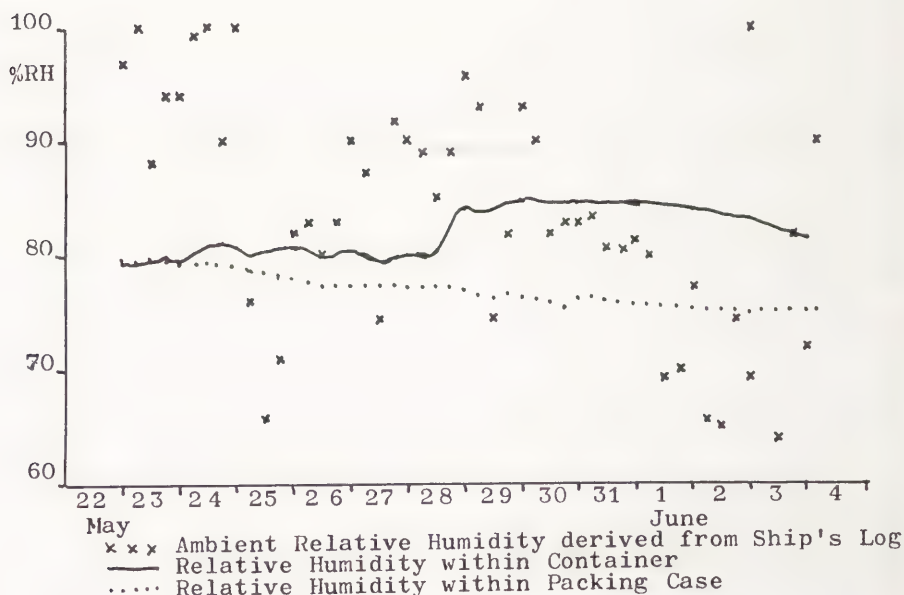


Fig. 4: Ambient Relative Humidity and the levels recorded within the Container and the Packing Case, 22 May - 4 June 1989.

Acknowledgements

The transportation of the Boucher tapestry cartoons from London to Muizenberg was organised by the author on behalf of Count N.A. D. Labia and the South African National Gallery, and the marine component was sponsored by Safmarine Ltd., but without the active assistance of the Master of S.A. Sederberg, Alexander Buchan, his Chief Officer, Rupert Travis, and their colleagues on board and in London, the project could not have been brought to a successful conclusion.

ABSTRACT

Measurements of relative humidity and temperature were made on the internal environment of a packing case used for shipping kimono objects between Japan and the United States. The moisture content of the silk fibres was calculated to increase by 1% on the outbound journey while decreasing by 5% on the return flight based on measurements of temperature and relative humidity inside the packing case. Actual ratios of RH variation to temperature variation during the two flights were 0.9 and 1.5. If the container were hermetically sealed, this ratio should, theoretically, worked out to 0.3. The lack of agreement between theory and practice indicates that the container was not entirely airtight. Moreover, the airtightness was further compromised on the return flight, causing even greater change in the moisture content.

KEYWORDS

transport, packing case, thermal insulation, airtightness, relative humidity, temperature, equilibrium moisture content, silk.

VARIATIONS IN RELATIVE HUMIDITY AND TEMPERATURE AS MEASURED IN A PACKING CASE

Nobuyuki KAMBA
Museum Science Department
National Museum of Japanese History
117 Jyonai-cho, Sakura-shi, Chiba 285
Japan

Introduction

The recent development of a compact solid-state memory recorder has facilitated measurement of changes in temperature and relative humidity within containers during transport. These data are useful in assessing the container's effectiveness in protecting its contents from environmental changes.

This paper discusses our experience in assessing a container used for shipping kimono objects between the National Museum of Japanese History, Japan and the North Carolina Museum of Art in the United States in 1988.

Environmental requirement for containers

Maintaining constant equilibrium moisture content (EMC) of museum objects during transport has been shown to prevent damage due to warping, shrinkage, and cracking. Toward this end, efforts have focused on increasing thermal insulation and airtightness and also incorporating moisture-buffering materials in order to achieve constant temperature and relative humidity inside the transport containers. This approach has been successful in achieving the constant EMC as long as the environment changes are minimal.

During transport, a container may, however, be subjected to significant and unexpected changes in the external environment--e.g., severe increase or decrease in temperature. The extent to which these changes will affect the internal environment of the container will depend on the provisions made to respond to these circumstances. The simpler and more effective approach is to focus on maintaining constant EMC of the object despite internal temperature and RH changes (rather than attempting to maintain constant RH in order to maintain EMC)[1].

Packing and Transport

1. Packing procedure and instrumentation

Like other Japanese museums, the National Museum of Japanese History has relied on packing containers provided by the transport companies for shipping museum objects; the packing case under discussion in this paper was no exception. The packing procedures and selection of packing materials described below were likewise designated by the shipper, per usual practice.

Each kimono object was first wrapped in thin pulp paper and placed on a corrugated paper board, then housed in a corrugated paper box along with two other pieces in the set. The packing case--constructed of 5-ply plywood, 10 mm thick--was designed to accommodate three of these boxes. Canvas-lined aluminium sheet material provided the interior lining, fitted with an additional layer of polyurethane foam to cushion the objects. No sealant was applied along the joint of the plywood. The interior volume of the empty case was 0.66 cubic meters. Nikkapellet, in the amount of 2 kg per cubic meter, was added to buffer the internal RH against changes in the external RH. With the case closed, minimal air space remained inside the case and boxes.

A compact solid-state memory recorder[2] with both temperature and RH sensors was mounted on the inner wall of the corrugated paper box positioned in the middle of the case. The recorder was set to take readings at 30-minute intervals.

2. Course of Travel

Once the objects were packed, the case remained for a few days in the packing area of the National Museum of Japanese History. Then, on 4 March 1988, the shipper transported it via truck specially outfitted for museum objects to Narita International Airport, where it then remained in a shed for about 24 hours. On the morning of 5 March it was loaded onto a Boeing 747 on a metal pallet. After a 13-hour flight, the plane landed at Dulles

International Airport in Washington, D.C. The case then proceeded by truck to the North Carolina Museum of Art, where it was unloaded into a storehouse upon arrival. This last leg of the journey took about 8 hours. Altogether, the journey lasted almost 2 days from beginning to end. Throughout the stay at the museum, the RH and temperature for the kimono objects were kept strictly regulated.

The return journey proceeded in almost the same manner. The case left the North Carolina Museum of Art on 1 July 1988 and arrived back at the National Museum of Japanese History on 2 of July without the 24-hour delay at Narita International Airport. The entire return trip took 30 hours.

RESULT

The temperature and relative humidity changes inside the case during transport are shown in figures 1 and 2 (See figs.1 and 2). These graphs show that the temperature changes corresponded directly to the relative humidity changes. During the outbound journey, the total temperature change was 13.8°C and the relative humidity change was 11.5%. During the return journey, the temperature change was 10.5°C, and the relative humidity change was 15.5%. The use of Nikkapellet buffer was not effective in maintaining constant internal relative humidity.

Fig.1 Temperature- and RH-recording during journey from National Museum of Japanese History, Japan, to North Carolina Museum of Art, the United States.

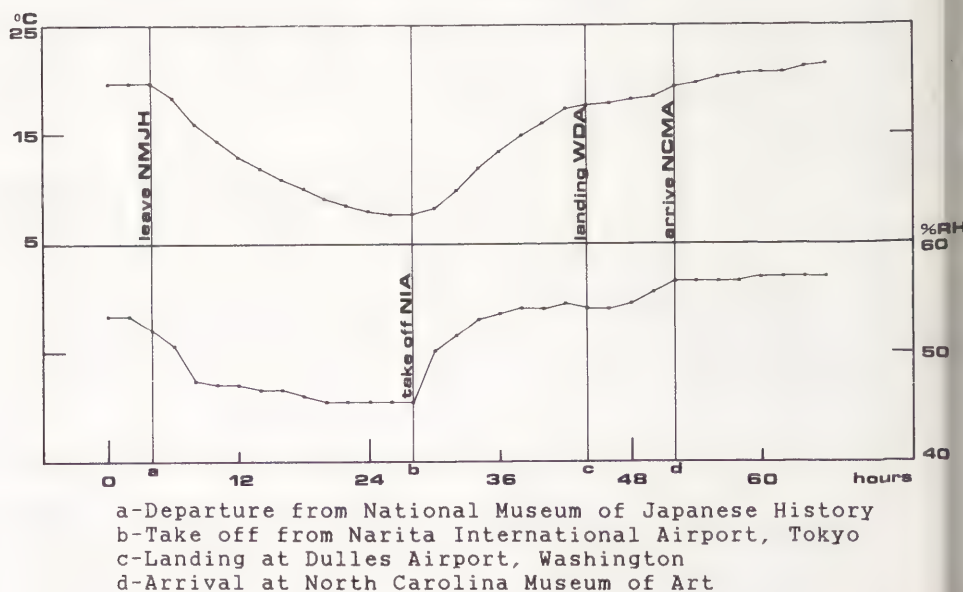
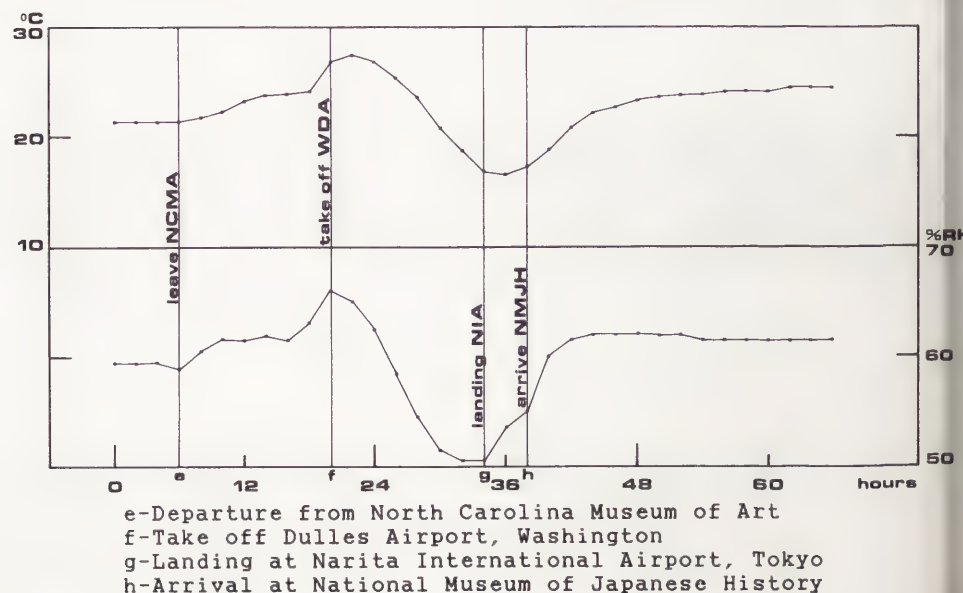


Fig.2 Temperature- and RH-recording during journey from North Carolina Museum of Art to National Museum of Japanese History.



Discussion

1. Changes in the moisture content of the silk fibres

Approximate RH and temperature relations for the different EMC of silk fibres[3] are shown in figures 3 and 4 (See figs.3 and 4). The vertical and horizontal axes represent RH and temperature respectively. Oblique lines indicating percentages of EMC are nearly parallel. Superimposed on these graphs are loop patterns showing the curves of changes of temperature and RH within the case during transport. These curves represent the moisture content of the silk fibres in the figures. As long as the curves run parallel to the lines of the EMC, the moisture in the fibres could be considered constant. It should be added, however, that this paper does not take response time of the fibres and packing materials into account. A time lapse occurs between changes in the environment and the response of the fibres in achieving a new equilibrium. Because of this lapse, the curves represented on the graphs do not represent strictly precise moisture content.

The loops indicate a hysteresis of the EMC of the materials within the case. Temperature and the RH change along the lower part of the loop as the materials loose their moisture; the opposite occurs along the upper part of the loop. Since both

Fig.3 Approximate RH and temperature relations for the different EMC of silk[3] and changes of temperature and RH during the outbound journey.

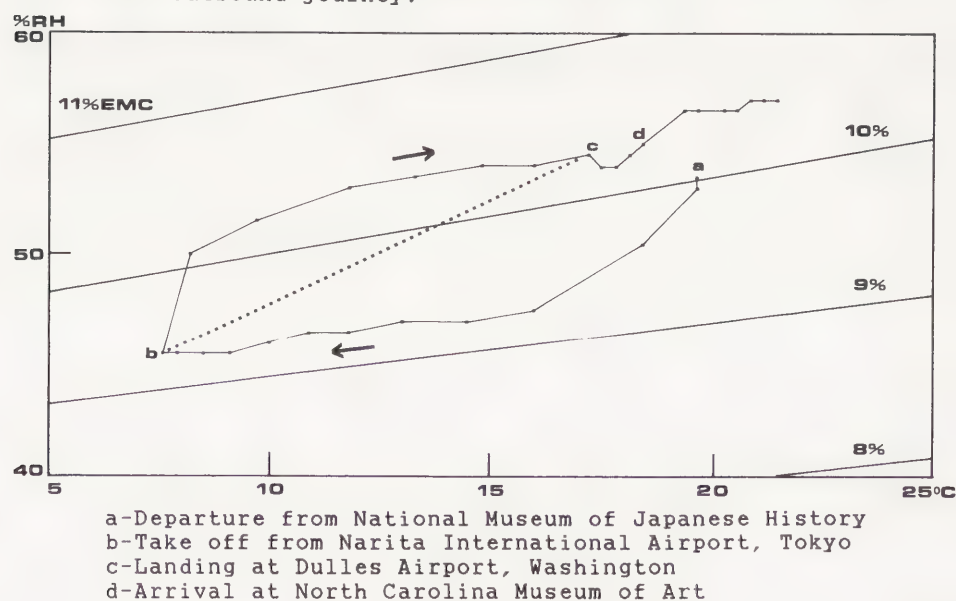
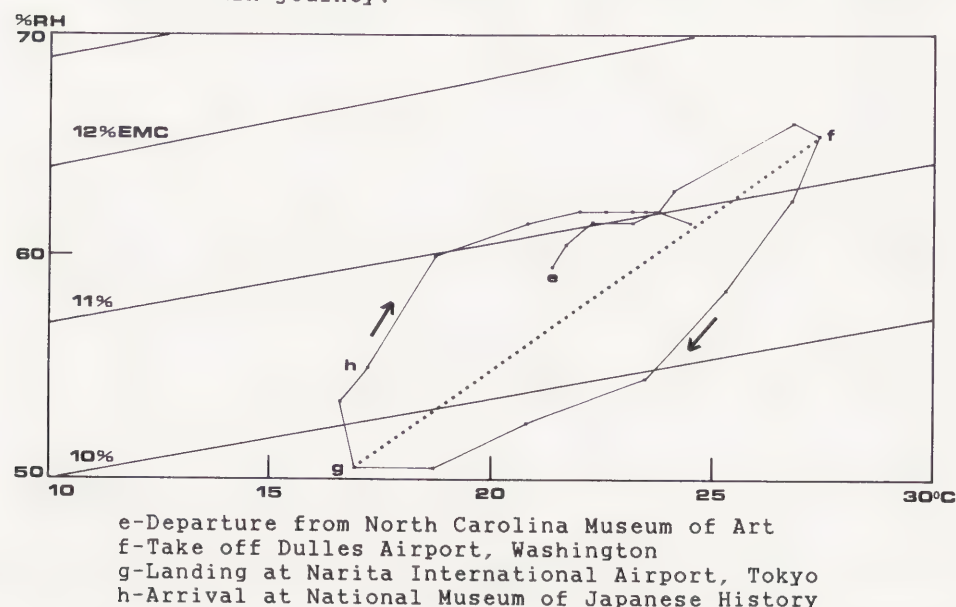


Fig.4 Approximate RH and temperature relations for the different EMC of silk[3] and changes of temperature and RH during the return journey.



loops are not parallel to the lines of the EMC, the moisture content of the silk fibres can be seen to have changed during transport. The moisture content increased 1% on the outbound flight from (b) to (c) as shown in figure 3; it decreased 1.5% during the return from (f) to (g), as shown in figure 4.

2. RH variation with temperature

The significant temperature change within the case indicate that the thermal insulation was not effective. The direct link between temperature changes and EMC changes is readily apparent. With respect to the relative humidity factor, we had assumed that the case was hermetically sealed, although no special provision had been made toward this end. Proceeding on this assumption, we had calculated the RH variation with respect to temperature using the method described by Thomson[4].

The case contained 7 kg of kimono objects, 20 kg of corrugated paper boxes, and 1.3 kg of Nikkapellet--that is, hygroscopic materials that exchange moisture with the air within the container. Initially, the materials in the container are in a state of equilibrium with the surrounded air at T °C and R %RH. Using Thomson's method, when temperature and the RH changed by ΔT and ΔR , the variations of the moisture content of the air ΔM_A and the materials ΔM_C in the case are:

$$\Delta M_A = \left(\frac{\partial M}{\partial T}\right)_A \Delta T + \left(\frac{\partial M}{\partial R}\right)_A \Delta R$$

$$\Delta M_C = \left(\frac{\partial M}{\partial T}\right)_C \Delta T + \left(\frac{\partial M}{\partial R}\right)_C \Delta R$$

If no moisture is gained or lost from the case, then:

$$\Delta M_A + \Delta M_C = 0$$

$$\therefore \Delta R = - \frac{\left(\frac{\partial M}{\partial T}\right)_A + \left(\frac{\partial M}{\partial T}\right)_C}{\left(\frac{\partial M}{\partial R}\right)_A + \left(\frac{\partial M}{\partial R}\right)_C} \Delta T$$

Thomson concluded that when the wood quantity exceeds 1 kg per 100 litres of air, the effect of air to the RH changes can be regarded as negligible. Even though the EMC values of materials such as silk fibres and paper are less than that of wood, about 4 kg of these materials per 100 litres air is sufficient to disregard $(\partial M/\partial T)_A$ and $(\partial M/\partial R)_A$ of the air. Thus:

$$\frac{\Delta R}{\Delta T} = - \frac{\left(\frac{\partial M}{\partial T}\right)_C}{\left(\frac{\partial M}{\partial R}\right)_C}$$

Table.1 Values of gradients of isobars $(\partial M/\partial T)$ and isotherms $(\partial M/\partial R)$ for various materials at 20 °C, 60%RH.

	silk[3]	wool[5]	Kraft paper[6]	cotton[5]	Nikkapellet[7]
$\frac{\partial M}{\partial T}$	-0.5	-1.0	--	-0.4	0
$\frac{\partial M}{\partial R}$	1.4	1.9	1.0	1.1	2.5

The units of $\partial M/\partial T$ and $\partial M/\partial R$ are g/Δ1 °C/kg and g/Δ1%RH/kg respectively.

In the above equation, $(\partial M/\partial R)_c$ and $(\partial M/\partial T)_c$ express the gradients of the equilibrium moisture content of materials at a constant temperature (isotherm) and RH (isobar) respectively. Values of the gradients of various materials are shown in Table 1. Since we have not accounted for the response time of materials to the environmental change, total values of the gradients of the materials in the case are expressed by adding each material's contribution to the gradients. Therefore:

$$\begin{aligned} \left(\frac{\partial M}{\partial T}\right)_c &= (-0.5) \times \frac{7}{28.3} + (-0.4) \times \frac{20}{28.3} + (0) \times \frac{1.3}{28.3} \\ &= -0.4 \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial M}{\partial R}\right)_c &= 1.4 \times \frac{7}{28.3} + 1.0 \times \frac{20}{28.3} + 2.5 \times \frac{1.3}{28.3} \\ &= 1.2 \end{aligned}$$

$$\therefore \frac{\Delta R}{\Delta T} = 0.3$$

We made an approximation of the gradients of the corrugated paper box using $\partial M/\partial R$ of Kraft paper and $\partial M/\partial T$ of a cotton fibre. Kimono is made mostly of silk. The value of $\Delta R/\Delta T$ obtained by theoretical calculation coincides with the gradient of the EMC of the silk fibres. Therefore, if the case is well sealed, the changes in temperature and RH inside the case will parallel the lines of EMC of the fibres and the moisture content of the silk fibres will remain constant.

The values of $\Delta R/\Delta T$ obtained using the measurement between (b) and (c) and between (f) and (g) are 0.9 and 1.5 respectively. This lack of agreement between theory and practice indicate that the case was not airtight. As the agreement between actual measurement and theoretical calculation improves, so does the airtightness of the container.

Conclusion

The poor thermal insulation of the packing case caused significant fluctuations of temperature inside the case, leading to RH fluctuations as well. As discussed above, the RH rose as temperature rose and vice versa.

We have likewise discussed fluctuations in the moisture content of the silk fibres using measurements indicating that our assumption--namely, that the case was hermetically sealed--was in error and that the penetration of external air increased on the return flight.

These results confirm that improvement of the thermal insulation and/or airtightness of the container are essential to keep the moisture content of museum objects constant during transport.

References

1. S. Hackney, "The dimensional stability of painting in transit", Preprints of 8th Triennial Meeting of ICOM Committee for Conservation, Sydney, 1987: 597-600.
2. Grant Squirrel Meter/Logger, Grant Instruments Ltd., Barrington, Cambridge, CB2 5QZ, England.
3. K. OGAWA, Seishi Gengyo Binran (Handbook of the silk reeling industry), (Tokyo: Meibundo, 1934), 75.
4. G. Thomson, "Relative humidity - variations with temperature of a case containing wood," Studies in Conservation 9(1964): 153-169.
5. Hariss Research Laboratory, Handbook of textile fibres, (Washington: Harris Research Laboratory Inc., 1954), 194-197.
6. Japanese Society of Polymers, Zairyo To Suibunn Handbook (Handbook of moisture within materials), (Tokyo: Kyoristu-Syuppan, 1968)
7. S. Weintraub, "Studies on the behavior of RH within an exhibition case. Part II: Measuring the effectiveness of sorbents for use in an enclosed showcase," Preprints of 6th Triennial Meeting of ICOM Committee for Conservation, Ottawa, 1981: 81/18/4

ABSTRACT

Packing case design is a critical factor when preparing delicate objects for transport. These objects must be protected from breakage and surface abrasion. The risks of abrasion can be minimized by carefully planned wrapping procedures. Foam cushions can be prepared for each packing case which provide the optimal protection from shock and vibration. The exact quantity of foam required for each case can be calculated using Dynamic Cushioning Curves. These techniques were successfully used for very delicate objects made of clay and terracotta in The Human Figure in Early Greek Art exhibition.

KEYWORDS

Packing, Packing cases, Clay, Terracotta, Dynamic cushioning curves, Foam

PACKING DELICATE ART OBJECTS FOR TRANSIT

Mervin J. Richard
National Gallery of Art
Washington, DC 20565

INTRODUCTION

The Human Figure in Early Greek Art was an exhibition organized by the National Gallery of Art, Washington and the Greek Ministry of Culture. It opened in January 1988 and traveled to The Nelson-Atkins Museum of Art in Kansas City, the Los Angeles County Museum of Art, The Art Institute of Chicago and the Museum of Fine Arts, Boston. The exhibition included sixty-seven objects dating from the tenth to the fifth centuries B.C., including sixty seen for the first time in the United States.

All of the antiquities in this exhibition were fragile, requiring meticulous attention to the packing and transport procedures. Those made from clay and terracotta, however, caused the greatest concern. Because of their fragility, these objects could easily be broken or abraded. Therefore, designing packing cases which would minimize the risks to the objects was a formidable challenge.

USING DYNAMIC CUSHIONING CURVES

One of the most important functions of a packing case is to isolate the object from shock and vibration. When cases are dropped, toppled, struck, rapidly accelerated, or rapidly decelerated, they are subjected to the exertion of force. If a packing case is properly designed, its cushioning materials, usually foam¹, will absorb most of the shock and vibration, transmitting only a small percentage of it to the object.

When a packing case is dropped, it accelerates until it strikes the floor. Immediately after impact, the motion of the packing case stops, but the contents inside the case move within the foam. If the foam is properly loaded, it compresses, slowly decelerating the contents as they sink into the foam. If the foam is too hard, it does not compress easily and the deceleration is very rapid. When the forces of deceleration are too great, the contents are damaged. If the foam is too soft, it compresses too easily and the contents move rapidly through the cushion until they strike the bottom of the case. On impact, the deceleration is very rapid and damage can occur.

As the scenarios described above indicate, the proper static loading of the foam used in packing cases is an extremely important consideration when optimal performance of the case is required. Packers routinely rely on experience, common sense, and intuition to select the most appropriate foam, its thickness, and the amount to use in the packing case. While this approach is usually successful, *dynamic cushioning curves* provide technical information that enables packers to make informed decisions about cushioning materials.

Dynamic cushioning curves have proven to be one of the most effective ways to evaluate a material's ability to isolate a packed object from shock. The data used for the curves is obtained by dropping a series of weights from a specific height onto a cushioning material. An electronic sensor, called an accelerometer, is used to measure the shock sustained by the various weights as they decelerate after striking the material. The rate of this deceleration is measured in G's. The probability of damaging an object increases as the number of G's exerted on it increases.

Test studies have shown that extremely delicate scientific instruments can be damaged by forces as low as 15 G's while large appliances such as refrigerators can withstand approximately 100 G's. Unfortunately, the specific number of G's required to damage art objects has not been determined. As a result, it is advisable to design packing cases that provide the best shock isolation possible within the existing financial and practical limitations.

Dynamic cushioning curves can be used to obtain the optimal performance from available packing materials. The curves for two thicknesses of polyester urethane foam² and one thickness of polyethylene foam³ are shown in Figure 1. Deceleration is given in G's on the Y axis and static loading, in kilograms per square centimeter, on the X axis. The data provided in Figure 1 is based on a drop height of 45 cm.

The practical application of cushioning curves is best explained by using an example. To simplify the description of the procedure, a hypothetical box measuring 30 cm x 30 cm x 30 cm and weighing 8 kg will be considered. As the fragility of the box is unknown, the objective in this example is to design a packing case that provides the best protection possible with the materials shown in Figure 1. The curves are surprisingly easy to use if a step-by-step procedure is followed.

Step 1: Select the materials for the packing case. In this example, it is assumed that 5 cm thick polyester urethane foam, 10 cm thick polyester urethane foam, and 10 cm thick polyethylene foam are the only cushioning materials that are available to the packer.

Step 2: Locate cushioning curves for the foams under consideration⁴. Note that the curves vary with drop height and foam thickness.

Step 3: Examine the curves and select the foam best able to provide the lowest deceleration value. In Figure 1, the lowest deceleration, 12 G's, is found on the curve for the 10 cm polyester urethane foam. It corresponds to a static loading of approximately 0.02 kg/cm². This shows that at a 0.02 kg/cm² static loading, a 12 G shock will be transmitted to the object if it is dropped from a 45 cm height. By comparison, the lowest deceleration for the 5 cm polyester urethane foam is approximately 28 G's and for the 10 cm polyethylene foam it is approximately 16 G's.

Step 4: Calculate the quantity, in square centimeters, of 10 cm polyurethane foam required to provide the optimal static loading of 0.02 kg/cm². The formula for this calculation is:

$$\begin{aligned}\text{Required Foam} &= \text{Weight of Object} \div \text{Optimal Static Loading} \\ &= 8 \text{ kg} \div 0.02 \text{ kg/cm}^2 \\ &= 400 \text{ cm}^2 \text{ (load bearing area)}\end{aligned}$$

This means that in the hypothetical packing case, 400 cm² of the foam should be placed on each side of the box.

Step 5: Design foam cushions that will safely support the hypothetical box using 400 cm² of foam on each side. In this example, each side of the box could be cushioned with one 400 cm² foam block, or two 200 cm² strips, or four 100 cm² foam blocks could be placed in the corners. It is important to understand that it would be a mistake to use a foam pad that covers the entire side of the box, an area of 900 cm². Too much foam can be just as damaging as too little foam.

While it would seem that any combination of cushions could be used, provided the total load bearing area equals 400 cm², in fact, a problem arises when the load bearing area of the cushions becomes too small relative to the thickness of the cushions. When the weight of a packed item is supported on cube-shaped or long slender foam blocks, the cushions have a tendency to compress non-uniformly. This phenomenon, called buckling, diminishes the effectiveness of the cushioning material. Buckling can be avoided if a simple rule is followed: the minimum load bearing area must be greater than or equal to the square of 1.33 times the thickness. Expressed mathematically:

$$\text{Minimum Load Bearing Area} = (1.33 \times \text{Foam Thickness})^2$$

In this example, where the foam thickness is 10 cm:

$$\begin{aligned}\text{Minimum Load Bearing Area} &= (1.33 \times 10 \text{ cm})^2 \\ &= (13.3 \text{ cm})^2 \\ &= 176.89 \text{ cm}^2\end{aligned}$$

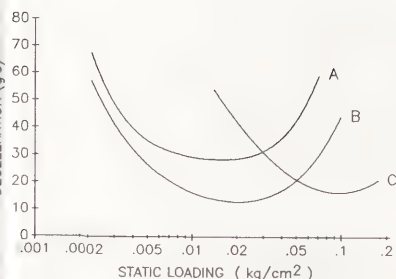


Fig. 1: Cushioning Curves for polyethylene and polyester urethane foams
(Drop Height = 45 cm;
Foam Density $\approx 32 \text{ kg/cm}^3$)

AA - 5 cm polyester urethane foam
BB - 10 cm polyester urethane foam
CC - 10 cm polyethylene foam

Therefore, the hypothetical box in the example could be appropriately supported with one 400 cm² or two 200 cm² foam blocks but not with four 100 cm² cushions. The latter cushions have a load bearing area considerably less than the calculated minimum of 176.89 cm² and they would buckle.

MINIMIZING SURFACE ABRASION

If foam cushions are properly designed, some movement of the packed contents is inevitable. For many art objects this movement is not a problem, however, those having extremely delicate surfaces can be abraded. Two approaches can be used to minimize the possibility of abrasion. First, a double case design may be used instead of a single case design. Second, special wrapping techniques may be used that allow the object to move without allowing the wrapping materials to rub against the surface of the object.

A single case packing system consists of an outer case, a cushioning material, and the object. The object is usually wrapped with tissue paper, fabric, or plastic sheeting. Calculations providing the proper static loading for the contents should be based on the weight and dimensions of the object in the case. It must be understood that if the static loading of the object on the foam is correct, it will move slightly during transit. In the double case approach, the object is held firmly within the inner case while that case is allowed to move within the foam of the outer case. Cushioning curves should be used to calculate only the quantity of foam required between the inner and outer cases. If the curves are used to calculate the quantity of foam required for the inner case, the object will move within the foam during transit. Unfortunately, the importance of holding the object firmly in place within the inner case is frequently misunderstood or ignored. As a result, objects are vulnerable to the same abrasion that can occur in a single case design; due to a phenomenon called tandem cushioning, the forces exerted on the object during transport can be magnified, exceeding the forces produced in a single case. It is essential, therefore, that the object be held firmly within the inner case.

A very successful method of holding small objects in place within the inner case is to fill the inner case with layers of foam and then cut an opening in the foam to match the contour of the object. The foam must be firm enough to hold the object securely in place. This procedure has several advantages: the object is held from all directions; the pressure required to hold the object is spread over its entire surface, thereby lessening the pressure exerted on any single point; and finally, the foam can be cut so that it does not contact particularly sensitive areas. The major disadvantage of this approach is that it can be very time consuming and requires a skilled packer to cut the foam.

Small objects can also be held in the inner case with a wrapping of bubble pack or wads of tissue. This procedure can be effective, but it requires careful manipulation of the materials by the packer each time the object is packed. It is also very difficult to avoid pressure on particularly sensitive areas. This procedure can be used safely on glazed ceramics, but it is not recommended for objects having soft surfaces, for example, painted terracotta or clay.

Filling the inner case with small polystyrene *peanuts*, or other polystyrene shapes is one of the simplest approaches, but it can have disastrous results if done improperly. The object is usually wrapped in tissue and then floated in the polystyrene peanuts. The procedure is very simple, fast and requires minimal skill. Unfortunately, the objects often move within the peanuts and can settle to the bottom of the case. It is also difficult to judge how many peanuts are required to obtain the optimal pressure against the object. If too much pressure is applied, the object can be damaged. If too little pressure is applied, considerable movement is possible and the surface can be abraded.

Regardless of how the object is held within the inner case, proper wrapping materials and techniques are required to minimize the risks of abrasion. The most frequently used wrapping material is acid-free tissue. With objects having hard surfaces, a fairly loose tissue wrapping is appropriate. With very delicate surfaces, a tighter wrapping is required since movement within loose tissue wrapping could cause abrasion.

WRAPPING TECHNIQUES

The repeated packing and unpacking required for the multiple venues of The Human Figure in Early Greek Art exhibition provided an excellent opportunity to perfect a wrapping technique that almost eliminated the risks of abrasion. The first time the objects were packed, they were loosely wrapped with tissue and placed in an inner box containing a mixture of polystyrene peanuts and other shapes. The inner box was then floated in an outer case cushioned with polyurethane foam on the bottom and polystyrene foam on the sides. While only a small amount of clay and pigment dust was found on the tissue when the objects were unpacked, even the slightest transfer of material to the tissue was unacceptable. It was concluded that a modified procedure was required for repacking the objects.

In the modified packing procedure, the polystyrene peanuts were eliminated and replaced with layers of foam. A soft polyurethane foam was used for very light objects and a harder polyethylene foam was used for heavier objects. A niche was cut in the foam to conform to the contour of each object. Considerable care was taken to avoid contact with particularly sensitive areas of the objects. Also, a gap was left between the object and the foam to allow for the substantial thickness of wrapping material.

The material selected for wrapping the objects was Archivart® Unbuffered tissue⁵. This product is a neutral pH, long-fibered tissue that resembles Japanese tissue papers. It is very soft, flexible, yet strong. The company sells it in sheets and in rolls. For this project, long rolls were purchased and cut into rolls having various widths.

The narrow rolls of tissue were used to slowly wrap the objects in a manner resembling the wrapping on Egyptian mummies. Nathan Stolow uses the term "cocoon" to describe this technique⁶. It was very important that the tissue be carefully laid on the surface without allowing it to slide against the surface during the wrapping procedure. If it slid, the movement of the tissue against the surface could have caused slight abrasion. It was also important that the tissue be held taut throughout the procedure so that it was not loose enough to slide during transit. As the layers of tissue were added, small strips of tape were used to hold the layers in place. While very little tape was used in the first repacking of the objects in this exhibition, experience showed that more tape than originally anticipated was required to hold the tissue layers in place.

This procedure was continued until ten or more layers of tissue covered the objects. In some areas, the complicated shape of the objects required that small squares, wads, or strips of tissue be laid against the surface before the *mummy wrap* proceeded. Also, sensitive areas on certain objects were left completely free of any tissue and the foam was cut to similarly avoid those areas. It was a time consuming and tedious process; some objects required three hours for the wrapping alone.

CONCLUSIONS

The combined use of the dynamic cushioning curves, a double packing case and the mummy wrapping technique proved very successful for the safe transport of the fragile objects in this exhibition. The tissue wrapping provided an outer skin for the object that protected its surface from abrasion. The objects were held firmly inside inner cases with layers of foam cut to match their contours. This ensured that objects could not move within the inner cases and that no pressure was applied to their most sensitive areas. Finally, the inner cases were floated within outer cases on polyurethane foam cushions. The static loading for the foam was carefully calculated for each inner case. This provided the optimal shock and vibration protection for the objects inside.

ACKNOWLEDGMENTS

I would like to thank the many individuals who, with tender loving care, packed the objects in The Human Figure in Early Greek Art exhibition. I would also like to express my appreciation to Janice Gruver, Shelley Sturman and Judith Brodie for their editorial assistance.

NOTES AND REFERENCES

1. To simplify the discussion, the word foam is being used instead of cushioning material.
2. The data for the curves was approximated from Graph 5.18 in the Military Standardization Handbook: Package Cushioning Design, MIL-HDBK-304B, (Washington, DC: Department of Defense, 1978), 231.
3. The data for the curve was approximated from the 10 cm (4 in) Ethafoam 220 curve in Fig. 4 of Product and Design Data for Ethafoam Brand Polyethylene Foam, (Midland, Michigan: Dow Chemical Company, 1984), 5. The company states that this data should not be taken as a specification for their product.
4. A good source for cushioning curves is: Military Standardization Handbook: Package Cushioning Design (see ref. 2). The curves are also available from some manufacturers.
5. Archivart® Division of Lindenmeyr Paper Company, Rutherford, New Jersey.
6. N. Stolow, Conservation and Exhibitions (London: Butterworths, 1987), 89.

ABSTRACT

The temperature and relative humidity inside packing cases during the transportation of works of art have been monitored using solid-state data loggers. The relative humidity has been found to be quite stable, regardless of changes in temperature which occur as the case equilibrates with external conditions. The thermal half-times calculated for a number of cases agree with those reported previously. The way in which the environmental stability is affected by the composition of the artifact and by variations in pressure during take-off and landing is explored.

KEYWORDS

Monitoring, Temperature, Relative humidity, Packing cases, Works of art, Transit, Data loggers.

MONITORING THE ENVIRONMENT WITHIN PACKING CASES CONTAINING WORKS OF ART IN TRANSIT

David Saunders
Scientific Department
The National Gallery
Trafalgar Square
London WC2N 5DN
England

Richard Clarke
Conservation Division
The National Maritime Museum
Greenwich
London SE10 9NF
England

INTRODUCTION

The function of a packing case is to protect works of art in transit from potential hazards. Case design has concentrated on isolating its contents from changes in the external environment, mainly changes of temperature and relative humidity, and from shock and vibration (1-3). Before a newly designed case is introduced, it is usual to perform a series of tests to ensure that external changes are adequately buffered (1,4).

Whilst data from these tests give a good indication of the likely performance of a packing case when it is subjected to adverse conditions, there have been only a limited number of studies conducted which seek to monitor the conditions within the case during routine journeys with works of art.

In this paper we deal exclusively with the monitoring of temperature and relative humidity. Earlier evaluations of performance under laboratory conditions have sometimes been complemented by an assessment of performance during one or two 'actual' transits (5,6). To date, there is only one published study of a significant number of journeys, conducted by the National Gallery of Art, Washington (7).

Over a period of two years the environment was monitored throughout twenty-three movements. The data comprised measurements made during journeys by road, some of which included ferry crossings, and by air. A few air journeys included intermediate take-offs and landings. The majority of transports were of paintings, a smaller number being scientific instruments from the National Maritime Museum. The paintings were transported in both the 'old' and 'new' versions of packing case described previously (4).

EQUIPMENT AND PROCEDURE

All the cases in which monitoring was carried out were of the same basic design. These cases have been used for painting transport by the National Gallery since 1982, and have subsequently been adopted by other museums and galleries including the National Maritime Museum. Particular features of these cases which make them suitable for the transport of works of art have been described elsewhere (4,5).

All measurements of temperature and relative humidity were made using a Vaisala combined temperature and relative humidity probe connected to a 'Squirrel' solid-state memory recorder (8). The 'Squirrel' logger has succeeded the Freeman Enercon memory recorder described in earlier experiments at the National Gallery (5). The 'Squirrel' data logger is particularly suitable for measurements inside packing cases since it is compact, uses a standard 9-volt battery, generates negligible heat and is relatively simple to operate. Furthermore, data from the logger are easily transferred to a personal computer for analysis and permanent storage.

There are a number of constraints which make recording conditions within cases during a 'real' art transport difficult: In the study conducted by the National Gallery of Art, around 25% of the journeys monitored were of empty cases (7). The major limitation is that of space within the case. For this reason, no data were collected for hand-carried shipments, where free space is minimal. Since temperature fluctuations in passenger areas are generally less severe than those to which cargo is subjected, it seemed reasonable to expect that conditions would have been better maintained in hand-carried cases. This supposition is borne out by the results of the Washington programme of monitoring (7).

A second, and important, limitation is the impracticality of measuring the external conditions during the journey. An external probe is easily damaged and, if it is to be connected to the logger within the case, there is a risk that the watertight seal might be compromised; the suggestion that a hole for a cable be made in a side panel was not well received. Despite this constraint it was often possible to make independent environmental measurements, although not usually in the cargo hold of an aircraft in flight. Details of take-off and landing times and of ambient conditions where possible were made by the courier accompanying each shipment.

The procedure followed for each of the monitoring experiments was similar. The 'Squirrel' logger was placed inside the case during packing. The position of the logger varied, but in each instance the device was surrounded by packing material to prevent it being dislodged during the journey. The probe was attached either to the inner surface of the packing material or, in certain experiments to determine if conditions differed across the polythene used to wrap the contents, to an unimportant part of the object, the backboard of a framed painting for instance. Care was taken to ensure that the tip of the probe was not obstructed. The 'Squirrel' was programmed to begin recording before commencement of the journey and the case was then sealed. In this way the equilibrium temperature and relative humidity within the case in the (hopefully) stable conditions of the packing room could be ascertained. The time interval between readings was chosen to give adequate coverage of changes in temperature and relative humidity without generating too much unnecessary and unwieldy data, or filling the available memory of the logger; the latter was rarely a problem.

After each monitoring experiment, data from the 'Squirrel' were transferred to a computer, stored permanently on disc and loaded into a spreadsheet programme for analysis (9). The use of a spreadsheet has allowed us to compare readings made in different cases during the same shipment, to produce graphs of temperature and relative humidity and to calculate other psychometric parameters from the recorded data.

RESULTS

Changes in Relative Humidity

The relative humidity inside the cases during transit was maintained within acceptable limits and with good stability. In the best instances the relative humidity remained within $\pm 1\%$ of the mean value. In over half the transports the relative humidity remained within $\pm 2\%$ of the mean value, except at take-off and landing; this phenomenon is discussed in greater detail below. Whilst the journeys during which the relative humidity remained most stable were not necessarily those in which the temperature remained constant, the largest variation of relative humidity, $\pm 5\%$, was measured during a transit by road in winter. Surprisingly, the problem in this instance was not that the vehicle was unheated, but that the packing case was moved into an icy corridor six hours prior to being loaded onto a vehicle with climate control.

The stability of relative humidity does not, however, imply that the equilibrium moisture content of the materials within a packing case will remain constant. Equilibrium moisture content is affected not only by relative humidity but also by fluctuations of temperature within the case (6). Changes of the magnitude measured during this study seem unlikely to cause significant damage to the objects as a result of changes in equilibrium moisture content.

Changes in Temperature

In accord with test results we found that the temperature within the packing case was less stable than the relative humidity. The rate of change of temperature varied from case to case; the surface area to volume ratio and thickness of insulating layer being important in determining the thermal response of each case.

It was, of course, not possible to reproduce during 'real' journeys the same temperature differences as in test situations. Neither were we able to measure the external temperature at all times. In many instances, however, the case has obviously reached equilibrium at the external temperature and it has been possible to calculate the temperature difference, and hence the thermal insulating efficiency of the case.

The relationship between rate of change of temperature and temperature difference is well established:

$$-dT/dt = k(T - T_{\infty})$$

T_{∞} = External temperature

T = Internal temperature at time t

T_0 = Initial internal temperature

k = Constant

t = Time

$$\text{thus : } \log_e((T - T_{\infty}) / (T_0 - T_{\infty})) = -kt$$

$$\text{and : } \log_e(T - T_{\infty}) = \log_e(T_0 - T_{\infty}) - kt$$

A plot of $\log_e(T - T_\infty)$ against time should, therefore, give a straight line with slope $-k$. It is then possible to calculate the half-time ($t_{1/2}$) for the case, i.e. the time for the temperature difference between the interior and exterior of the case to halve, using the relationship:

$$t_{1/2} = \log_e(2) / k = 0.693 / k$$

The longer the half-time, the better the thermal insulation of the case. Fig. 1 illustrates the close correlation between the temperature decrease within a case during a shipment by road and the theoretical prediction of internal temperature based on a particular thermal half life.

Old style cases, those of the type in use since 1982, were found to have thermal half-times between 3½ and 4½ hours. The new style of case for painting transport was found to have a half-time in the region of 6 hours. This latter figure agrees well with the thermal half-time obtained from laboratory heating and cooling of the new style case (4).

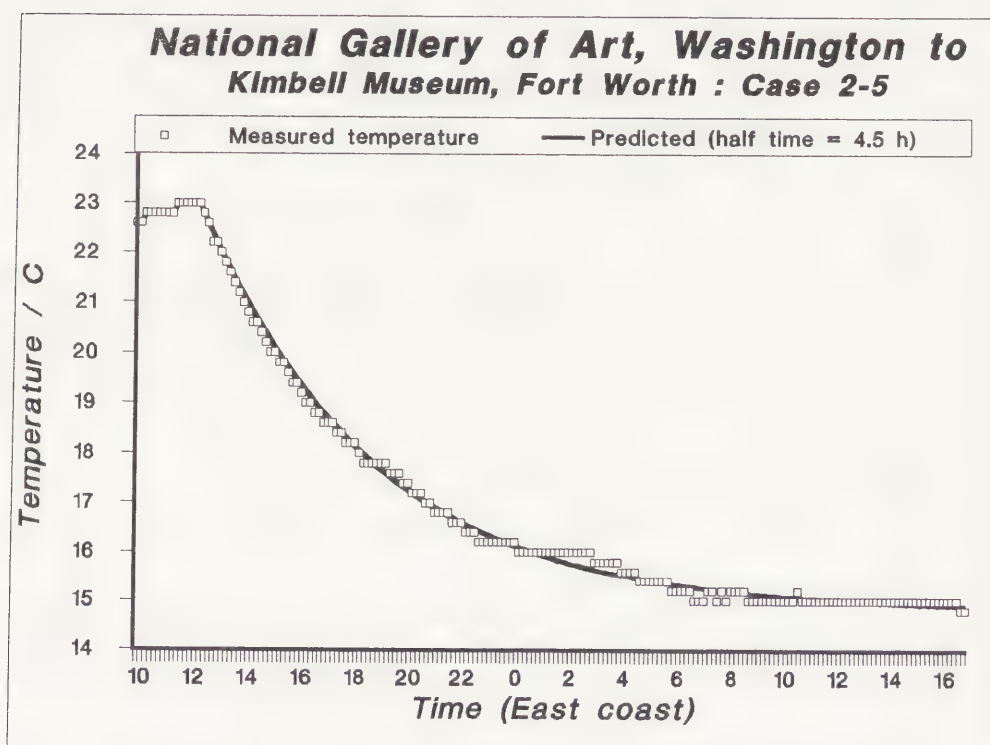


Fig. 1. Graph of temperature against time for a shipment in winter by road. The boxes indicate the measured temperature, the solid line represents the predicted temperature assuming a thermal half-time of 4.5 hours.

Results suggest that objects in transit are most at risk from changes in temperature and relative humidity at the time of unpacking. The first hazard occurs if a case is unpacked soon after arrival at the receiving institution, before the temperature has had time to equilibrate with ambient conditions. If the relative humidity and temperature in the room are high, so that the temperature of the object is below the dew point, moisture may condense on its surface. For instance, if the temperature and relative humidity in the room where an object is unpacked are 22.5°C and 55% respectively, the dew point temperature will be approximately 13°C. It is not inconceivable that an artifact arriving during winter in a vehicle without climate control will be at a temperature of 13°C or less. From the temperature decrease shown in Fig. 1, we concluded that contrary to expectation, a non-conditioned vehicle had been used for this journey.

Ideally, the case should be left to equilibrate in the room in which it will be unpacked. Paradoxically, the more efficient the thermal buffering of the case, the longer this period of equilibration will need to be. Twenty-four hours is generally recommended. This is equivalent to around four thermal half-times for the most efficient case. Thus even a 16°C temperature difference should have been reduced to around 1°C over this time.

A second problem emphasised by our findings, although well recognised previously, is the discrepancy between conditions in packing rooms at different institutions. In the absence of rapid changes of temperature, the relative humidity inside the case tends to stabilize at the same level as during packing. Even if thermal equilibrium between the case and the room in which unpacking is to take place has been reached, it is possible that the relative humidity will be different. This is exemplified in Fig. 2. After a journey by road and ferry, the case was left overnight to equilibrate. During this time the relative humidity stabilized at around 48%, the same as that at the time of packing. It is clear, however, that the room into which the object was unpacked was at a somewhat higher relative humidity, around 56%. This change in relative humidity is far larger than any change during the journey and is very sudden. In this instance it seems that the temperature outside the case was also different to that immediately before unpacking. Since the temperature had clearly reached equilibrium, this implies that the case was stored overnight in a different room to that in which it was subsequently unpacked.

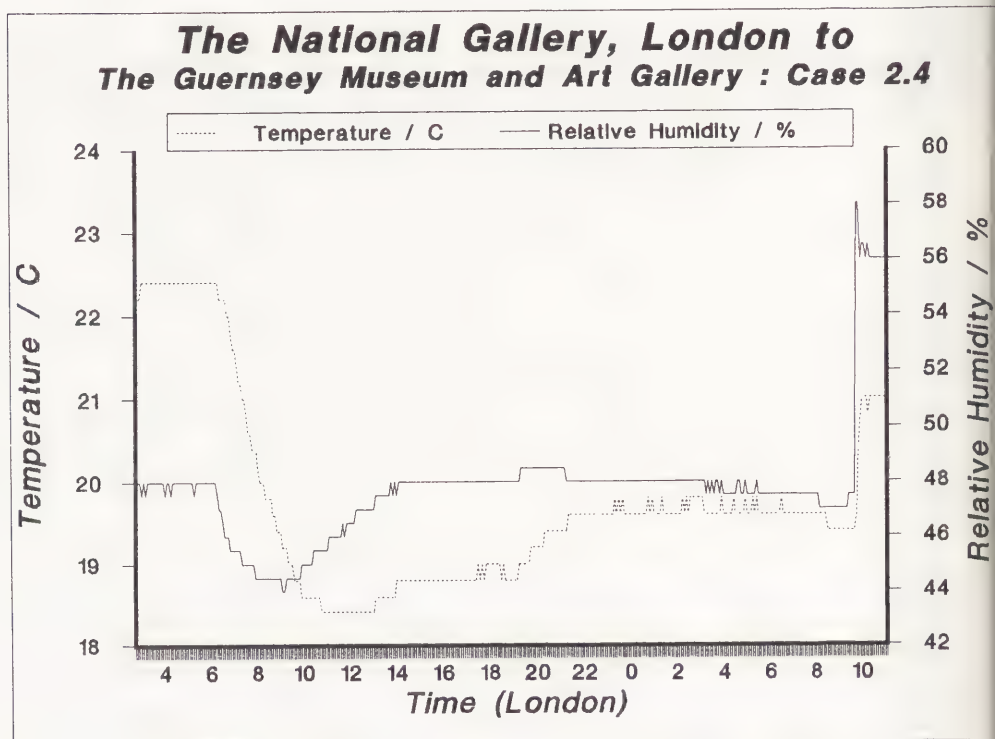


Fig. 2. Graphs of temperature and relative humidity against time for a journey by road and ferry.

Behaviour on take-off and landing

Sudden changes in relative humidity at take-off and landing have been attributed to changes in pressure as an aircraft climbs to cruising altitude and descends prior to landing (10). Available information indicates that the pressure in cargo holds during flight decreases to around $0.75 - 0.85 \times 10^5 \text{ Nm}^{-2}$ (6,11,12). It has been suggested that changes in relative humidity occur because air is extracted from the case as the pressure decreases on take-off, to be replaced by air from the cargo hold on landing (6). It is generally agreed that the relative humidity in cargo holds is in the region 10 - 25% (7,13). If dry air were to enter the case on landing, one might expect to observe a decrease in relative humidity. In all the air transports where sudden changes in relative humidity were noted, the relative humidity increased immediately prior to landing, having decreased soon after take-off. Depending upon the length of flight and the temperature, the relative humidity during the course of the air journey usually stabilized to a level slightly lower than that prior to take-off. This pattern of behaviour is well illustrated by the measurements of relative humidity made inside a case during a typical journey by air (Fig. 3).

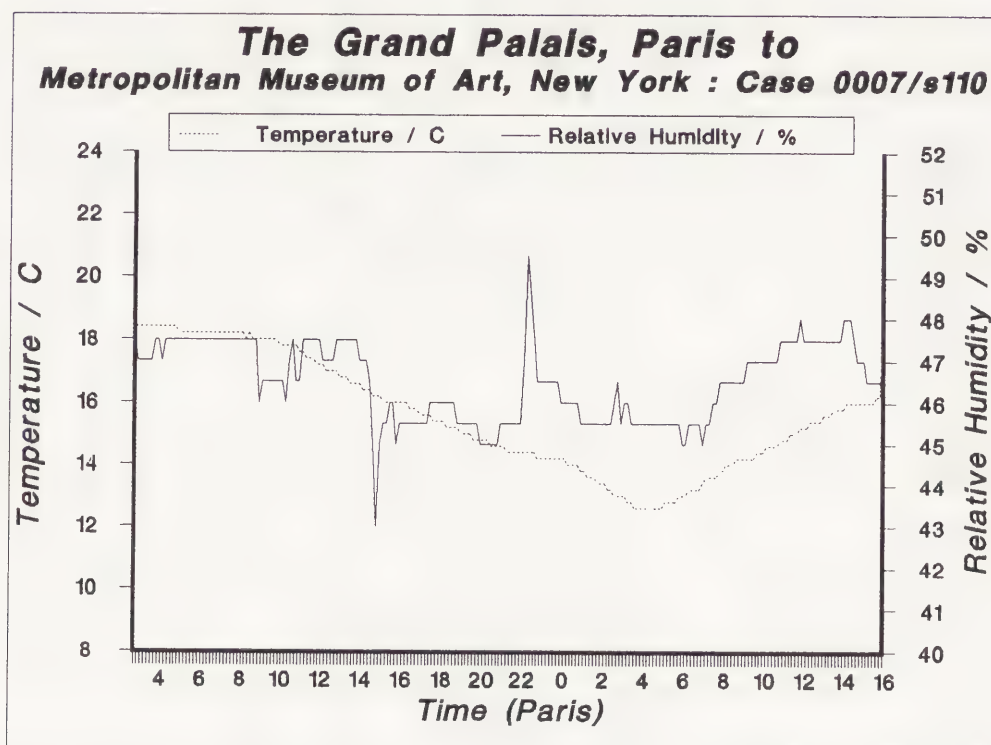


Fig. 3. Graphs of temperature and relative humidity against time for a journey by air: Take-off from Paris was at 14:40, landing in New York at 22:50.

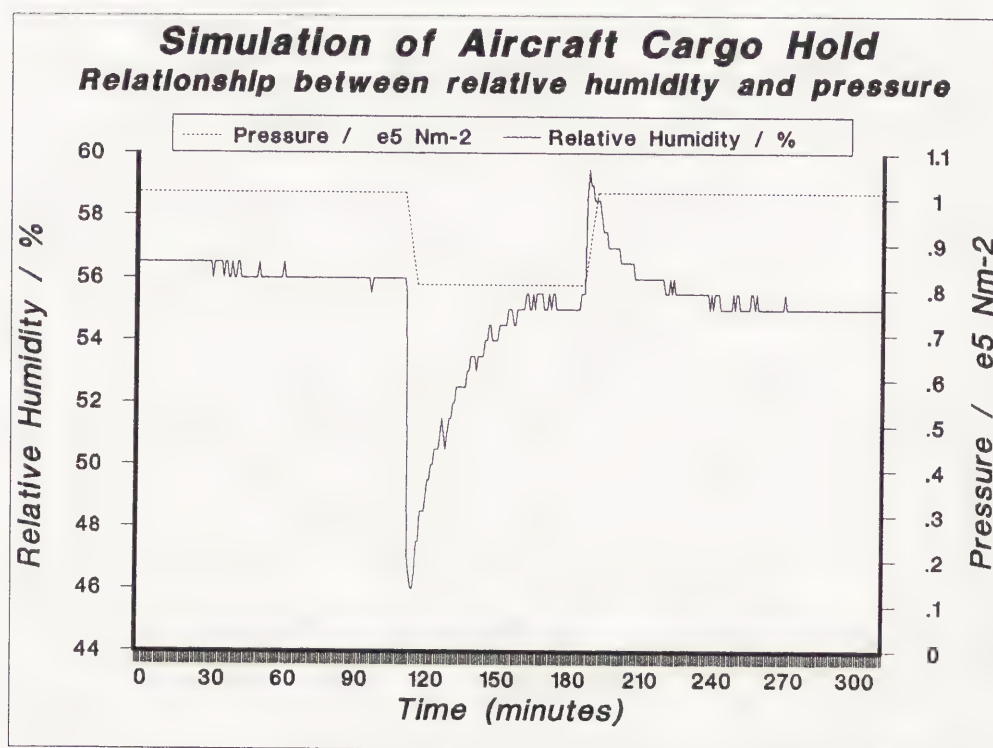


Fig. 4. Graph of relative humidity against time during a simulation of pressure changes in an aircraft cargo hold.

It is known that relative humidity is not independent of pressure; indeed it has been predicted that misleading readings of relative humidity may be obtained from psychometric tables if pressure is ignored (11). In order to test our theory that the phenomenon is caused by pressure change rather than by an exchange of air between case and hold, a 'Squirrel' logging device was placed in a vacuum chamber within an air-conditioned space. Several bags of silica gel were placed in the chamber and allowed to equilibrate to the relative humidity of the surrounding space, 56%, for forty-eight hours. The chamber was then sealed. After three hours the pressure in the chamber was reduced to $c. 0.8 \times 10^5 \text{ Nm}^{-2}$. After a further hour, the pressure was allowed to return to atmospheric pressure by allowing air from the surrounding space to enter. The chamber was sealed again and left for three hours before the 'Squirrel' was removed and switched off. During the course of the experiment the temperature and relative humidity in the surrounding space remained at $23.2 \pm 0.2^\circ\text{C}$ and $56.0 \pm 0.5\%$ respectively.

A plot of relative humidity against time, illustrated in Fig. 4, shows a similar pattern to that found in 'real' transports, agreeing well with the data plotted in Fig. 3. The results suggest that pressure change alone may be the cause of these phenomena.

The nature of the contents

The stability of relative humidity in cases used for the transport of paintings has been attributed to the presence of large volumes of buffering material, principally wood, compared to a much smaller air volume within the case (6,14). During a number of earlier experiments, we had placed probes both outside and inside the polythene sheet in which paintings are wrapped prior to packing. The results had indicated that the relative humidity did not significantly differ across this sheet. Presumably, the relative humidity inside is buffered by the wood in the painting's frame, whilst the packing materials act as a moisture reservoir for the air outside the wrapping. We were interested to see how stable the environment would be within cases containing inorganic art objects. The transport of a number of scientific instruments from the National Maritime Museum to Australia for a series of exhibitions offered such an opportunity.

Fig. 5 illustrates the variation of temperature and relative humidity within two cases during the transport of exhibits from the Mitchell Library, Sydney to the National Maritime Museum, London. Case 10 contained a framed painting, whilst Case 30 contained a selection of scientific instruments. The figure shows broadly similar temperature variations within the two cases. The temperature dropped on leaving the museum in the antipodean winter, rose during the stop-over at Bangkok, then decreased again during the subsequent flight. Finally, on arrival in London on a warm summer day the temperature rose. The results suggest that Case 30 was placed in a slightly warmer part of the hold during the flight.

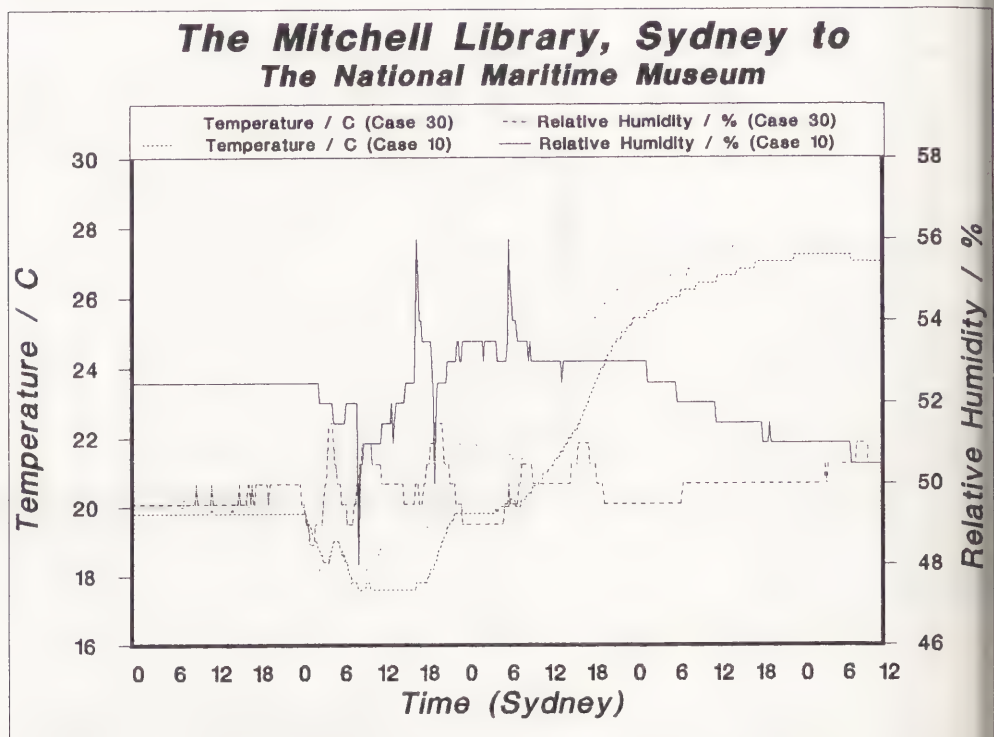


Fig. 5. Graphs of temperature and relative humidity against time for a journey by air from Sydney to London via Bangkok: Take-off from Sydney was at 07:00, landing in Bangkok at 15:00; take-off from Bangkok was at 19:00, landing in London at 05:00.

In a similar way, fluctuations in relative humidity are small in both cases. The results for case 10 show the relative humidity changes associated with take-off in Sydney and Bangkok and landing in Bangkok and London. The pressure change does not seem to be reflected in the results for case 30, perhaps the seals on this case were more effective. Excluding the changes on take-off and landing, the change in relative humidity is less than $\pm 2\%$. These small changes suggest that the ratio of packing material to free air in the case (7 : 1) is sufficient to give adequate moisture buffering in the absence of organic materials in the object.

CONCLUSIONS

Within experimental limits relative humidity within packing cases during actual journeys is stable. The presence of organic materials only produces a small improvement in this stability. Changes in relative humidity during take-off and landing may be attributed to pressure changes rather than to movement of air in and out of cases. The temperature is less stable, since the internal temperature moves towards equilibrium with the surrounding air. The thermal insulation properties of the cases accord well with experimental results obtained previously, the improved version of the case having a longer thermal half-time.

It is clear that cases should be allowed sufficient time to equilibrate before unpacking, perhaps 24 hours, and that the relative humidity during packing and unpacking should be matched if possible. Furthermore, the use of conditioned vehicles will eliminate some of the more extreme variations, particularly in temperature. Where available, heated aircraft cargo holds might be used.

The results have shown the 'Squirrel' data logger to be an effective method of monitoring conditions in packing cases during transit.

ACKNOWLEDGEMENTS

Ann Stephenson-Wright, David Fellowes, and all the couriers from the National Maritime Museum and National Gallery who faithfully recorded transit details.

REFERENCES

1. Stolow, N., Care of Works of Art in Transit and on Exhibition: Review and Assessment. Preprints of the International Council of Museums Committee for Conservation, 6th triennial meeting, Ottawa, 1981, 81/12/1.
2. Staniforth, S., The Testing of Packing Cases for the Transport of Paintings. Reprints of the International Council of Museums Committee for Conservation, 7th triennial meeting, Copenhagen, 1984, 84/12/7.
3. Green, T. and Hackney, S., The Evaluation of a Packing Case for Paintings. Reprints of the International Council of Museums Committee for Conservation, 7th triennial meeting, Copenhagen, 1984, 84/12/1.
4. Stephenson-Wright, A. and White, R., Packing: An Updated Design, Reviewed and Tested. National Gallery Technical Bulletin, 1987, 11, 36.
5. Staniforth, S., Packing: A Case Study. National Gallery Technical Bulletin, 1984, 8, 53.
6. Hackney, S., The Dimensional Stability of Paintings in Transit. Reprints of the International Council of Museums Committee for Conservation, 8th triennial meeting, Sydney, 1987, 597.
7. Merrill, R. M., In the Service of Exhibitions: The History. Problems and Potential Solutions of Cultural Materials in Transit. Reprints of the American Institute for Conservation, 16th annual meeting, New Orleans, 1988, 138.
8. The 'Squirrel' solid-state memory recorders, type SQ32 and MQ32, were supplied by Grant Instruments of Cambridge, England.
9. Results were analyzed and graphs produced using the SuperCalc5 spreadsheet package from Computer Associates.
10. Staniforth, S., Packing of Two-dimensional Objects (Paintings, Prints and Drawings). Reprints of the UKIC one day meeting "Packing Cases - Safer Transport for Museum Objects" London, 1985, 10.

11. Karp, C., Calculating Atmospheric Humidity. Studies in Conservation, 1983, 28, 24.
12. Martin, G., Preliminary results of research at the Victoria and Albert Museum, London, Personal communication, 1989.
13. Toishi, K., Jet Transport of Art Objects. in Museum Climatology, ed. G. Thomson, IIC London Conference, 1967, 41.
14. Thomson, G., Relative Humidity Variations with Temperature in a Case Containing Wood. Studies in Conservation, 1984, 9, 153.

THE COURIER EXPERIENCE

Shelley G. Sturman* and Judy L. Ozone
Object Conservation Department
National Gallery of Art
Washington, D.C. 20565 USA

Introduction

The National Gallery of Art (herein referred to as NGA) has an international reputation for its special exhibitions - both for their grand scale and frequency of scheduling. In other words, there is always something big happening at the museum. John Buchanan, Registrar at the Metropolitan Museum in New York, pointed out that "with the dramatic increase in special exhibitions that has continued unabated since the late 1960s has come an equally dramatic increase in courier traffic, aptly described by a colleague as a 'growth industry'."¹ The role of the courier has become an important part of the museum's operations to ensure the safe transport of valuable objects loaned to other institutions. A courier may be required for a number of reasons:

1. To oversee the handling of museum objects that are fragile due to their nature, manufacture, size, materials, condition;
2. To safeguard objects that are irreplaceable or of unique quality, including those that are politically and culturally sensitive;
3. To assist with those objects that require special handling or have unusual installation requirements;
4. To protect objects during the course of complex transportation arrangements;
5. To minimize careless handling, excessive movement, changes in environment, or other hazards.²

Although either the lending or borrowing museum may require a courier, it is the lending museum that makes the final determination of the need for a courier before approving a loan. However, in the words of Peter Canon-Brookes,

No useful purpose is served in sending an escort or courier who has not been properly trained to carry out what is often a very demanding role, or who travels unprepared. Lack of understanding of the function of escorts and couriers, and the limits of their authority, is the cause of more confusion than almost any other element in the transportation of works of art, and consequently a rich source of misunderstandings and friction between exhibition organizers and lenders.³

With these facts in mind and with the continual rise in the annual number of couriered objects, the NGA's registrar and conservation departments developed a courier training program. The goal is for every potential courier to become versed in the responsibilities and demands required of the courier. The experience has been positive for those leading the program as well as for the eventual couriers; the program is offered approximately twice a year.

The Courier

The primary responsibility of a courier is to ensure the safe transport of the object to its destination. The courier is the agent of the NGA, with full authority to act in protection of the couriered object until officially released to the borrowing museum. Only staff who have intimate knowledge in the handling of works of art and understanding of the condition of the object and its special requirements are eligible to courier objects. Generally, courier duties are limited to curators, conservators, registrars, and senior art handlers. Each staff member must complete a domestic courier trip before the assignment of an international trip. All are required to attend periodic sessions of the courier training program.

*Author to whom correspondence should be addressed.

The Courier Training Program

The half-day session is jointly presented by the registrar and conservation departments. One of the purposes of the training session is to give the courier an idea of what to expect while traveling alone with the art object. A picture of the process is painted through a slide presentation and the recounting of others' experiences. Each section is described in detail and illustrated with sample forms and diagrams where applicable.

The agenda covers a number of topics:

1. Courier responsibilities
2. Travel papers
3. Conservation considerations
4. Packing/unpacking
5. Hand-carried shipments
6. Cargo shipments
7. Questions

1. Review of Courier Responsibilities

During this portion of the training session, the registrar carefully reviews a number of underlying principles and guidelines for the courier. For each trip, an individual registrar works with the courier from the planning stage through the follow-up of the trip. This gives the courier an idea of the itinerary, the personnel with whom (s)he will be in contact, and what might be expected during the course of travel.

A courier does not discuss information about the trip with anyone except on a justified need-to-know basis. Travel cannot include family or friends. If a vacation is planned, others join the courier once the object has been formally delivered.

Before couriership any object, the conservator and curator have previously determined that the object is safe for travel. The courier must familiarize him/herself with the object, together with the conservator, conservation condition report, and photographs. The courier is alerted to any potential problem areas such as weak joins, fragile or projecting parts, and any irregularities that previously existed. Information regarding the individual artwork's acclimatization requirements is also provided. (S)he is responsible for knowing about any special problems with the object or transit and must be able to convey any special handling, display, or security instructions to the borrower.

The moment the object leaves the museum, the accompanying courier is expected to operate on behalf of the museum. The courier is authorized to take any action needed to protect the object while it is in his/her care.

The courier observes the loading of the object onto the truck and travels with the object to the airport (or train station). Once at the airport, (s)he observes the unloading as well. Upon arrival at the borrowing institution, the courier designates when the crate can be opened. The courier supervises the unpacking, instructing the responsible staff on the proper sequence. The object is examined jointly with a staff member and the courier's incoming condition report is reviewed, preferably by a conservator. As long as the borrowing institution holds the object, it also retains a copy of the condition report.

The courier (and not the receiving registrar, exhibition curator, or security chief) is in charge of the object until it is unpacked, proper security is provided, and receipts and condition reports are signed.⁴

The courier should know where the object is to be installed for exhibition. If it is not to be installed immediately, a satisfactory storage place should be found. In both cases, the courier should be happy with the locations and conditions. When the object is safely placed and the courier is given a signed receipt and condition report, his or her responsibility can be considered completed.

2. Preparation of In-House Travel Papers

The program introduces the potential courier to the paperwork that initiates the travel process. The traveler is responsible for preparing and submitting to the museum administration the authorization papers that justify and account for the time and money expended for the courier trip. Estimates for air and ground travel, lodging, subsistence, and miscellaneous expenses are included. The *per diem* is based on published federal government rates. A certain amount of money can be advanced to the traveler. Air travel is arranged through a government travel agency and tickets are generally billed directly to the museum. After the trip, an accounting of expenses with the corresponding receipts is submitted. Expenses (less any money advanced) are reimbursed to the traveler. The total is then billed to the borrower. The NGA has a strict policy that prohibits the courier from accepting any money on site from the borrowing institution.

Other forms submitted prior to departure are the application for administrative leave and an application for overtime, if extra hours of work are anticipated.

3. Role of the Conservator

The conservator's role begins in the earliest stages of the loan procedure. When first requested by a borrower, the object is initially examined by a conservator to determine its stability and if it is safe to travel. A conservator's detailed examination can disclose condition problems that are not readily apparent and a treatment will be proposed that will prepare the object for the loan. The conservator is instrumental in making recommendations on handling, packing, and exhibition conditions. If then approved for loan by the museum administration, negotiations and conditions for loan are pursued. A factor that is key in determining the loan approval is the environmental conditions at the borrowing institution. Changes in temperature and humidity as well as continual fluctuations can have irreversible effects on the work of art. Many changes that take place in an object may not manifest themselves immediately.⁵ Prior to the loan approval, the NGA requests a written report from the borrowing institution that describes physical and environmental conditions, including information on fire suppression systems.

In the event of damage, the registrar from the lending museum is notified immediately. Careful and complete notes together with detailed photographs are taken. The original condition report is annotated and initialed by both the courier and the borrower's representative. A record of the circumstances and personnel involved is included. A borrowing institution may wish to repair damage or perform minor treatment to an object, but in no case should a courier allow them to treat an NGA object without receiving approval from the proper NGA personnel, even in a case as simple as removing a frame.

4. Packing and Unpacking

The loan objects are packed by experienced art handlers in accordance with accepted practice, conservation requirements, and carrier regulations. The courier is responsible for witnessing and supervising packing, unpacking after the acclimatization period, removal for installation or to secure area, and examination of the object at the beginning and end of shipment. Since borrowing institutions may contract packing to a commercial firm, it is especially crucial to closely supervise repacking procedures. Complex packing may require a diagram or photograph to assist the courier and borrower during unpacking and repacking. Familiarity with the work of art allows for greater packing ease since there will be few surprises when the courier is away from the museum and the aid of registrar and conservator.

Humidity sensitive objects may travel in specially constructed cases that serve as both packing and exhibition cases. Through the use of silica gel in the case, a micro-environment can be created and maintained throughout transport and duration of the loan. The courier is required to should be familiar with the specifications of the silica gel and case since (s)he will probably be responsible for explaining its function to the borrower.

5. Details of Hand-Carried Shipments

The courier must have the physical strength to hand-carry the object packed in its case. Personal luggage cannot be carried together with the hand-carried work of art. The program discusses specifics of several modes of transportation. An automobile courier must be accompanied by a second individual at all times and the shipment must never be left unattended. A public conveyance courier must be escorted to departing train or airplane by museum personnel or designated agents. Hand-carried objects are placed under the seat in front or strapped into a purchased seat, but never in an overhead bin. If the pilot is agreeable, the cockpit is also an acceptable location for a hand-carry during flight. The object must never be surrendered to baggage. The courier should try to prevent the opening of crates for customs inspection or in any public area.

6. Procedural Details of Air Cargo Shipments

The majority of objects transported by air are carried in the cargo compartment of the airplane. They can be secured on a pallet, in a closed container, or strapped directly to an interior wall of the cargo compartment. This means that the object is out of view of the courier for much of the time. Courier observation is often limited to the time during which it is in holding at the cargo terminal. It is important to do whatever is possible to ensure the safety of the object. It is the courier's responsibility to make sure that no hazardous or liquid materials or live animals are put on the pallet or in the container with the art object. The pallet or crate is then wrapped in plastic to protect it from moisture. The crate must be securely strapped and well balanced on the pallet or in the container.

If at all possible, the pallet, container, or crate is observed as it is transported and loaded onto the aircraft. Note the pallet or container number. A copy of the air waybill is obtained from the customs broker (or forwarding agent) before departure. This paperwork relates the courier to the object being shipped.⁶

If the courier is not able to accompany the object to planeside, the forwarding agent will serve as the observer. Once the object leaves the cargo terminal, it is up to the agent to apprise the courier of its location and status. The agent must know that the object is not to be left outdoors for long periods of time, especially in rain, snow, extreme heat, or extreme cold. The agent should be able to tell the courier where the object is located on the aircraft.⁷

Once on the aircraft, the courier can ask the purser about any changes in the object's location, should there be any stops or problems. Refer to the pallet or container number when making inquiries.

When the plane lands, the courier is met at the airport by a staff member from the borrowing institution or by a customs agent who will expedite clearing the object from customs. As with loading, the courier or agent observes the offloading and handling of the crate. After the object is released, the courier takes an active role once again by supervising the loading of the object onto the truck en route to the borrowing institution.

Summary

Each courier experience is unique. If the courier knows the object well and remains responsible for that object at all times, there should be few problems. The objective of the courier training program is to familiarize the courier with his/her responsibilities and obligations to the object and the National Gallery of Art. By reviewing previous courier situations and having joint discussions with registrars, conservators, and art handlers, the courier is able to make a well-informed decision and minimize potential problems.

Glossary of Paperwork⁸

1. NGA Outgoing Receipt--identifies borrowing museum, mode of transport, objects being shipped, exhibition and dates, outgoing receipt number. Must be signed by representative of the borrowing institution and returned to NGA.
2. Conservation Condition Report and Annotated Photograph or Drawing--indicates object accession information, borrower, packing method, special instructions, and details of object's condition including frame, base, or mounting method.
3. Letter to carrier for hand-carry objects--names courier and object being hand-carried, requests that package not be unwrapped or submitted to x-radiography, testifies that no weapons are concealed.
4. Airline Air Waybill/Bill of Lading/Airbill--identifies shipper, consignee, nature of shipment, flight information, shipment number, payment. The courier must always have a copy of the air waybill or have its number. Additionally, the courier must record the pallet or container number and its position on the plane.
5. Trucker's Bill of Lading--indicates shipper, consignee, crates being shipped, shipment reference number, payment. These are usually signed by a representative of the registrar's department at pick-up and delivery.
6. *Pro-forma* invoice--prepared by NGA for use by customs broker, indicating the objects in shipment, value, purpose, shipper, consignee. The courier must always carry the pro-forma invoice. It is critical to have this document on arrival in a foreign country, especially with hand-carried objects.
7. Customs broker and customs documents--various documents required by the airlines and by U.S. and foreign customs to identify the shipment and its value and the nature of the customs entry. This document is usually given to the courier by the forwarding agent for delivery to the receiving agent.
8. List of names, with work and home telephone numbers and addresses where appropriate, of all the agents, museum personnel, and shippers who are involved with the transaction and could be of assistance.

Notes

1. John Buchanan, "The Courier's Art," Museum News 63, #3 (1985): 11-18.
2. Virginia Mann, Edward Quick, et al., "A Code of Practice for Couriers of Museum Objects," (prepared by the Registrar's Subcommittee for Professional Practices, The American Association of Museums, June 1986), 4.
3. Peter Cannon-Brookes, "A Draft Code of Practice for Escorts and Couriers," The International Journal of Museum Management and Curatorship 1, #1, (1982): 41-60.
4. Buchanan, "The Courier's Art," 13.
5. Ann Hoeningswald, "Courier Guidelines from a Conservator's Point of View," NGA Courier Training Session, 1988.
6. Mary Suzor, Anne Halpern, and Judy Cline, "NGA Courier Information," handout for National Gallery of Art Courier Training Session, 1988.
7. Dorothy Dudley, Irma Wilkinson, et al., Museum Registration Methods, third edition, revised, American Association of Museums, Washington, D.C. (1979): 137.
8. Mary Suzor, Anne Halpern, and Judy Cline, "Glossary II: Glossary of Paperwork," handout for National Gallery of Art Courier Training Session, 1988.

1. The first part of the report is a general introduction to the subject of the study. It discusses the importance of the problem and the objectives of the research.

2. The second part of the report is a detailed description of the methods used in the study. It includes a discussion of the experimental design, the data collection procedures, and the statistical analysis.

3. The third part of the report is a presentation of the results of the study. It includes a discussion of the findings and their implications for the field of research.

4. The fourth part of the report is a conclusion and a discussion of the limitations of the study. It also includes a list of references and a bibliography.

5. The fifth part of the report is a summary of the main findings of the study. It includes a discussion of the implications of the results and a list of recommendations for further research.

6. The sixth part of the report is a list of references and a bibliography. It includes a list of the sources used in the study and a list of the works cited in the report.

7. The seventh part of the report is a list of appendices. It includes a list of the supplementary materials that are provided with the report.

8. The eighth part of the report is a list of figures and tables. It includes a list of the visual aids that are used in the report.

9. The ninth part of the report is a list of footnotes. It includes a list of the notes that are provided at the bottom of the report.

10. The tenth part of the report is a list of references and a bibliography. It includes a list of the sources used in the study and a list of the works cited in the report.

11. The eleventh part of the report is a list of appendices. It includes a list of the supplementary materials that are provided with the report.

12. The twelfth part of the report is a list of figures and tables. It includes a list of the visual aids that are used in the report.

13. The thirteenth part of the report is a list of footnotes. It includes a list of the notes that are provided at the bottom of the report.

14. The fourteenth part of the report is a list of references and a bibliography. It includes a list of the sources used in the study and a list of the works cited in the report.

15. The fifteenth part of the report is a list of appendices. It includes a list of the supplementary materials that are provided with the report.

16. The sixteenth part of the report is a list of figures and tables. It includes a list of the visual aids that are used in the report.

17. The seventeenth part of the report is a list of footnotes. It includes a list of the notes that are provided at the bottom of the report.

18. The eighteenth part of the report is a list of references and a bibliography. It includes a list of the sources used in the study and a list of the works cited in the report.



GETTY CENTER LIBRARY



3 3125 00003 1134

Working Groups

Page	1	Scientific Examination of Works of Art
	105	Structural Restoration of Paintings on Canvas
	149	Ethnographic Materials
	179	Documentation
	209	Modern and Contemporary Art
	227	Wet Organic Archaeological Materials
	247	Photographic Records
	275	Textiles
	319	Stone
	371	Theory and History of Restoration
	399	Care of Works of Art in Transit